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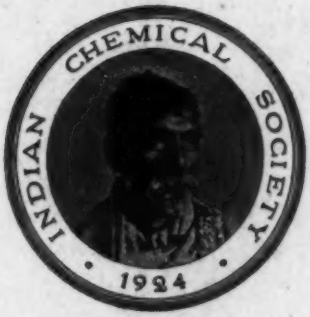


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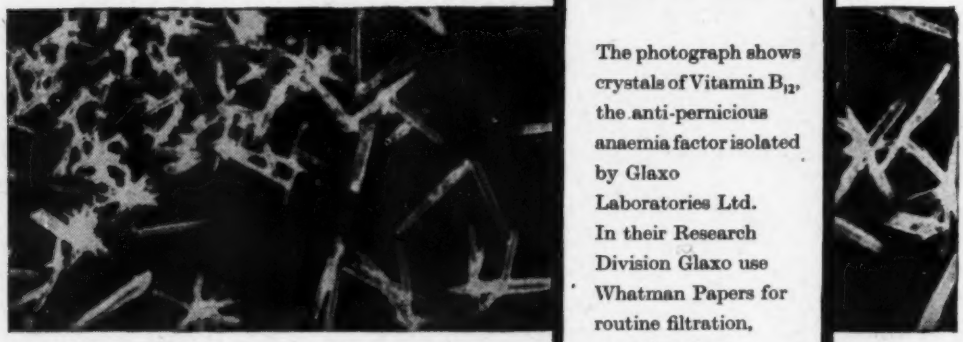

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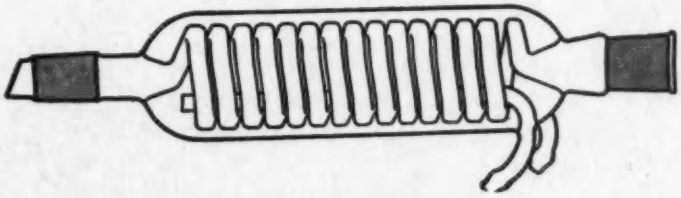

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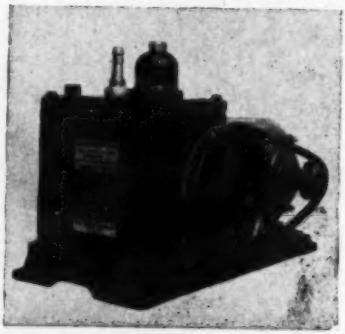

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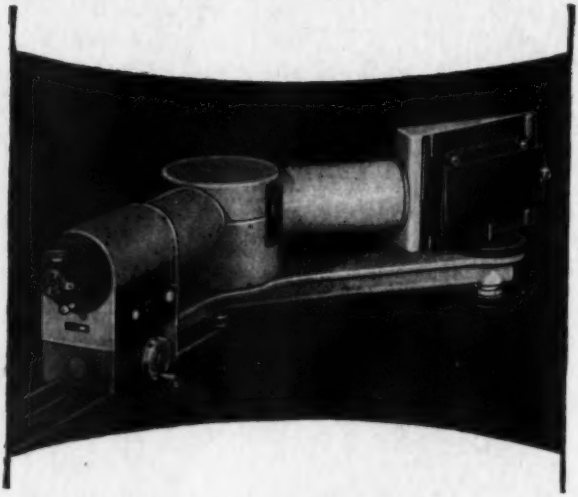

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[Jour. Indian Chem. Soc., Vol. 37, No. 9, 1960]

# THERMALLY STABLE CO-ORDINATION POLYMER. PART I. METAL THIOSEMICARBAZONE OF NAPHTHAZARIN

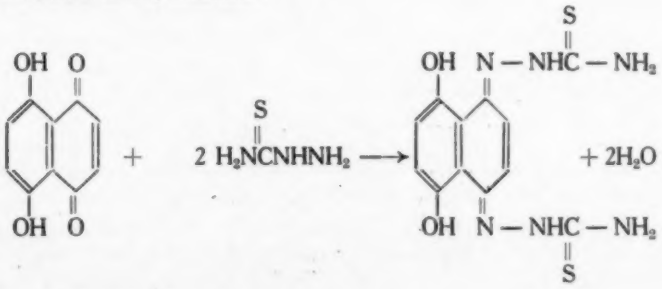
By D. N. Chakravarty* and W. C. Drinkard

For the first time the metal co-ordination polymer of thiosemicarbazone has been synthesised. Thiosemicarbazone of naphthazarin and bivalent hexa-co-ordinating metal ions, like zinc or nickel, comprise the recurring group of the above copolymer. This group of co-ordination polymers is found to possess high thermal stability, indicated by differential thermal analysis. Unique thermal stability is shown by the zinc thiosemicarbazone of naphthazarin which starts slight decomposition at 450°.

Polymers containing a metal ion, bonded to an organic ligand, may have unusual thermal properties endowed by the metal ion. During the past five years an increased interest has been shown for the production of the co-ordination polymer in an attempt to obtain polymeric substances of high thermal stability. Copper phthalocyanine, which sublimes undecomposed at 500° (Dent and Linstead, *J. Chem. Soc.*, 1934, 1027) is found to be a successful case of co-ordination polymer, and has been thoroughly investigated (Bailer, Drinkard and Judd, Technical Report, WADC, U.S.A., No. 57-391; Lawton and McRitchio, *ibid.*, No. 57-642). Several other examples of high thermal stability have been reported for polymers formed by joining polyfunctional ligands by chelation to a metal ion, but molecular weights have been estimated to be quite low. The low molecular weight of the polymer might be attributed, in part, to the extreme insolubility of the complex which results in precipitation of the polymer before chain growth can occur. By taking extreme precautions the authors have been able to prepare co-ordination polymer, metal dimercaptals (Chakravarty and Drinkard, 136th American Chemical Society Proceeding Abstract, p. 14 N, 1959) which have molecular weights in the vicinity of 6000. In the present case an attempt has been made to prepare a co-ordination polymer by taking low molecular weight, polyfunctional ligand and complexing them with suitable metal ions. Polymerisation of this type is achieved when steric factors prevent co-ordination of all donor groups of a molecule with a single metal ion. Thus, metal acts as a bridging group between polydentate ligands.

Thiosemicarbazone, formed by the reaction of naphthazarin with thiosemicarbazide, is found to act as a bidentate chelating ligand for metal ion, like Cu (II), Zn(II), Ni(II), and the thiosemicarbazone acts as a bridge between ions. Thus, a polymer chain grows through consecutive thiosemicarbazone—metal linkage.

Naphthazarin (5:8-dihydroxy-1:4-naphthaquinone) is found to be a suitable diketone in affording a thiosemicarbazone, as shown :

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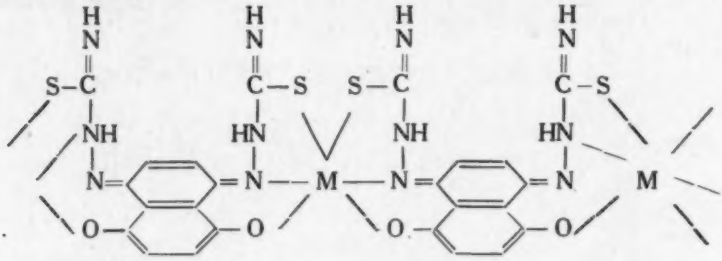
The product may act as a *bis*-tridentate ligand. Steric factor prevents all six positions from co-ordinating to a single metal ion. Addition of a bivalent hexa-co-ordinate ion would be expected to produce the polymer shown below.



Loss of proton produces a polymer with no charge. The Zn(II) and Ni(II) complexes have been prepared in dimethylformamide solution. The infusible black powders form as precipitates. Differential thermal analysis indicates in some places no decomposition up to 400°. Insolubility of the product prevents molecular weight determination.

## EXPERIMENTAL

*Copper Naphthazarin Complex.*—A solution of cupric chloride (0.53g., 0.003 *M*), naphthazarin (0.57 g., 0.003*M*), and triethylamine (68 g., 0.006 *M*) in 25 c.c. of absolute ethanol was refluxed for 1 hour. The reaction mixture was allowed to stand overnight and the blue solid was removed by filtration. The complex was dried at 110°. (Found : Cu, 21.5. $Cu_4C_{50}H_{22}O_{20}$ requires Cu, 21.4%).

End group titration indicates an equivalent weight of 643. If the two end groups are phenol, a molecular weight of 1286 is indicated.

*Naphthazarin Thiosemicarbazone.*—Naphthazarin (3.8 g., 0.02 *M*) and thiosemicarbazide (3.6 g., 0.04 *M*) were dissolved in 30 c.c. of *NN'*-dimethylformamide, and refluxed for 2 hours. The solution was cooled to room temperature and the black precipitate of naphthazarin thiosemicarbazone was filtered. The product was washed with ethanol and dried. The sample was impure. (Found : C, 46.4; H, 2.74. $C_{12}H_{12}O_2N_6S_2$ requires C, 42.8; H, 3.6%).

*Zinc Thiosemicarbazone of Naphthazarin.*—A suspension of naphthazarin (1.9 g., 0.01 *M*) was refluxed in 30 c.c. of 1 *M*-NaOH till complete solution. Thiosemicarbazide (1.8 g., 0.02 *M*) in ethanol and powdered zinc acetate dihydrate (2.2 g., 0.02 *M*) were added. The mixture was refluxed for 3 hours. During the reflux period the deep blue solution gradually changed to black in colour and the precipitate of zinc thiosemicarbazone naphthazarin appeared. The precipitate was filtered, washed with 95% ethanol, and dried at 110°. [Found : C, 37.76; H, 2.62; Zn, 18.35. $(ZnC_{12}H_8N_6O_2S_2)_n$ requires C, 36.0; H, 2.5; Zn, 16.3%).

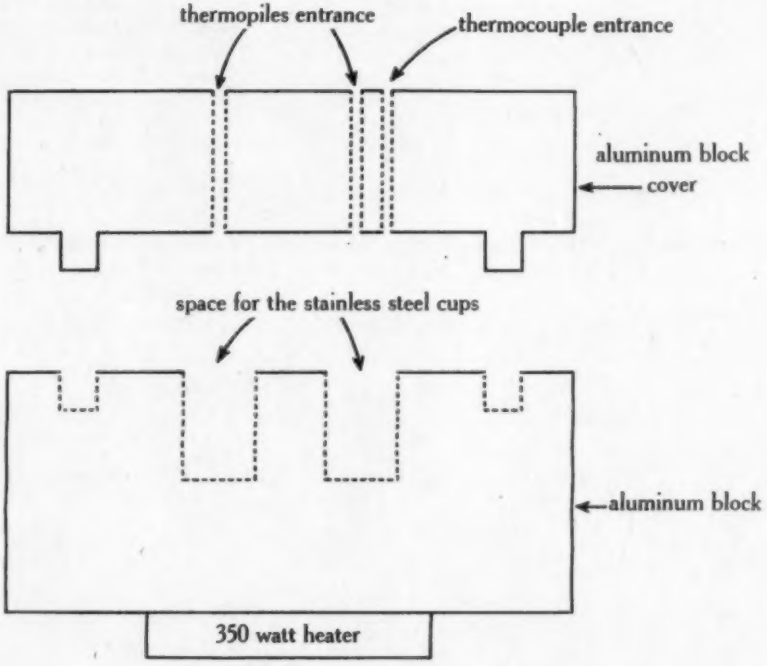
*Nickel Thiosemicarbazone of Naphthazarin.*—Nickel formate (1.8 g., 0.01 *M*) in ethanol (20 c.c.) was mixed with a solution of naphthazarin (1.9 g., 0.01 *M*) and thiosemicarbazide (1.8 g., 0.02 *M*) in 20 c.c. of *NN'*-dimethylformamide. The mixture was refluxed for 2 hours. The precipitate of nickel thiosemicarbazone of naphthazarin was filtered, washed with ethanol, and dried at 110°. [Found : C, 37.7; H, 8.5; Ni, 11.6. $(NiC_{12}H_8O_2N_6S_2)_n$ requires C, 36.9; H, 8.2 ; Ni, 15.0%].

*Thermal Stability Measurements*

Unless otherwise stated, the thermal stability of all samples was determined by differential thermal analysis. D.T.A. equipment has been constructed in this laboratory.

Samples were contained in two identical, thin wall, stainless steel cups. Aluminium oxide was used as the standard inert sample and as the diluent for the unknown. A standard sample of 2.0 g. of $Al_2O_3$ was balanced against a sample of 0.1 g. of the compound in 1.9 g. of $Al_2O_3$.

*Sample heating.*—Samples were heated in an aluminium block by a 350 watt heater as shown in Fig. 1.




Maximum temperature is limited by the m.p. of the aluminium. Heating rates were varied between 8° and 2° per minute by use of a variac.

*Temperature Measurement.*—The differential temperature was measured by two thermopiles of four, iron-constantan thermocouples inside a thin-wall capillary. Absolute temperature was measured by a single iron-constantan thermocouple placed in the sample. The thermocouple was protected by a thin-wall glass capillary. The system was standardised against the crystal structure change of $NH_4Cl$, which occurs at 184.3°.

*Temperature Recorder.*—Both absolute and differential temperatures were recorded by a Brown, 2-point, automatic recording potentiometer. The absolute scale was extended by inclusion of a "buck out" potential from a Rubicon Co. potentiometer.

Differential temperature of 0.02° may be determined. Absolute temperature may be determined to 0.5°.

*Sample Atmosphere.*—No attempt was made to control the atmosphere above the sample. Access to the air was restricted, however, by the $Al_2O_3$ diluent and the aluminium cover.

*Differential Plots.*—The decomposition peaks are very broad, usually extended for several minutes. Maximum stability was taken as the point of initial rise of differential plot. Peak maxima usually occurred at a temperature approximately 10° higher than the initial break.

*Decomposition Point.*—Decomposition point of the compounds, as recorded by the D.T.A. set up described above, are presented in Table I.

TABLE I

| No. | Compounds. | Point of D.T. change. |
|---|---|---|
| 1. | Copper naphthazarin complex | 355° |
| 2. | Naphthazarin thiosemicarbazone | 320° |
| 3. | Zinc thiosemicarbazone of naphthazarin | 450° |
| 4. | Nickel thiosemicarbazone of naphthazarin | 400° |

The authors wish to thank the U.S. Borax Research Corp. for its support of this investigation.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
LOS ANGELES, U.S.A.

*Received April 27, 1960.*

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# ION-EXCHANGE REACTIONS WITH HETEROIONIC SYNTHETIC RESINS. PART I. CATION EXCHANGE

BY L. POCHHALI

Ion-exchange reactions with a cation-exchange resin, saturated with two different types of cations at different degree of saturation, against a third type of cation in solution have been studied by the equilibrium method. The exchange of the more replaceable ion has been found to be enhanced and that of the less replaceable ion suppressed; this interaction increases with the degree of saturation of the complementary ion. It has also been shown that the order of introduction of the ions in the resin during the preparation of the heteroionic resin salts has no influence on the release of the two ions. The variation of the selectivity coefficient for the ion, added against the two ions originally present in the resin, with their degrees of saturation has also been pointed out.

When an ion exchanger, saturated with two different types of ions, say A and B, is treated with a salt solution containing a third type of ion, C, the exchangeability of A and B is quite different from that when the exchanger in pure A-form or pure B-form is treated with the C-salt solution separately. This shows that one ion affects the exchangeability of another, and an ionic interaction exists in ion-exchange reactions. The earlier investigations were generally concerned with the relation between the degree of saturation of the exchanger with respect to a particular cation and its exchangeability mainly with heteroionic clays (Horner, *Missouri Agr. Expt. Sta. Res. Bull.*, 1936, No. 1 232; Marshall, *ibid.*, 1944, No. 1 385; Yarussov, *Pedology*, 1938, **6**, 799; Mehlich and Colwell, *Soil Sci. Soc. Amer. Proc.*, 1943, **8**, 179; *Soil Sci.*, 1946, **61**, 369; Allaway, *ibid.*, 1945, **59**, 207 et seq).

Weisz (Dessertation, Budapest, 1932), Yarussov (*Soil Sci.*, 1937, **43**, 285) and Schachtschabel (*Koll. Beih.*, 1940, **51**, 199) from their studies on ion exchange with heteroionic clay minerals conclude that the exchangeability of a cation decreases as the proportion of the complementary cation increases in the clay minerals. The same opinion is held by Jenny and Ayers (*Soil Sci.*, 1939, **48**, 443). They have calculated on the basis of Jenny's (*J. Phys. Chem.*, 1936, **40**, 501) picture of the ion-exchange reaction that in a system of A-B-clay+C-salt, the exchangeability of A approaches zero as the proportion of B, the complementary ion, increases in proportion to A. They also found that the influence of the nature of this complementary cation, B, was highly significant. Thus, for instance, in the case of K-Ca, K-$NH_4$ and K-Na clays, the exchangeability of $K^+$ at the same saturation in the different systems decreases in the order $Ca > NH_4 < Na$.

Bray (*J. Amer. Chem. Soc.*, 1942, **64**, 954) on the other hand held an essentially different opinion. He asserts that the exchangeability of a cation is not determined by its degree of saturation but by its own ability of release, and by the nature of the complementary cation. From replacement experiments with natural soils and HCl he obtained constants which he considered as a measure of the relative exchangeability of the cations.

Wiklander (*Ann. Roy. Agr. Coll.*, Sweden, 1946, **14**, 1) discussed these different view points and considered in some detail the influence of complementary ions in exchange reactions. On the basis of the law of mass action and the activity concept, he derived some equations for computing the release of ions saturating the exchanger. These equations are in fair agreement, at least qualitatively, with his experimental results. He showed that the percentage replacement of an ion was dependent partly on the nature of the ion, partly on the nature of the complementary ion, and

partly on the degree of saturation with the ions in question. The percentage replacement of an ion, say M, may increase, remain constant, or decrease as the degree of saturation with M is decreased. If the activity coefficient of M ( $f_m$ ) is greater than that of the complementary ion, $f_c$, the percentage replacement of M increases ; the latter remains unaltered if $f_m = f_c$, and decreases if $f_m < f_c$. If the saturating ions are dissimilar in valency, the one of lower valency is released in greater amounts, and that of the higher valency in smaller amounts as the degree of saturation decreases. Wiklander took different types of ion exchangers, e.g., clay, permutite and synthetic ion-exchange resins, both cationic and anionic, but in all his experiments he exchanged the saturating ions with very dilute HCl.

The exchangeability of an ion from a heteroionic exchanger depends also on the mode of preparation of the ion exchanger, as has been shown by Renold (*Koll. Beih.*, 1936, **43,** 1), and Mukherjee (*Bull. Indian Soc. Soil Sci.*, 1942, **4,** 1). This may be illustrated by the following experiment. A mixed K-Ca clay containing the same equivalent amounts of the two cations is prepared in one experiment by adding $Ca(OH)_2$ first and then KOH, and in another experiment by adding KOH first and then $Ca(OH)_2$. Exchange measurements of $K^+$ and $Ca^{2+}$ against a third cation show that the amount of $K^+$ exchanged from the first heteroionic clay is greater than that from the second, whereas $Ca^{2+}$ is exchanged in less amount from the first than from the second. Mukherjee (*ibid.*, 1944, **6,** 19), and Ganguli and Mukherjee (*J. Phys. Coll. Chem.*, 1952, **56,** 56) have further shown that there are distinct critical ratios for the mono and bivalent cations at which these differences in exchangeability are observed. Thus, for instance, in a Na-K clay, the difference in exchangeability of $Na^+$ in the two clays, Na-K-clay and K-Na-clay, is not noticeable until the proportion of $Na^+$ in the clay exceeds 30%. The same is true of $K^+$ also. But for bivalent cations this critical proportion was found to be (~) 50%.

The present paper attempts to collect some more observations about the exchange reactions with heteroionic exchangers and mainly deals with the effect of the degree of saturation on the exchangeability of an ion from a cation-exchange synthetic resin, saturated with two different types of cations. As the symmetry values for different ions can suitably characterise the ion-exchange reactions (Jenny, *J. Phys. Chem.*, 1932, **36,** 2217), the ions were exchanged by a third cation added at its symmetry concentration, *i.e.*, the amount of the cation added was always kept equivalent to the total amount of ions originally present in the resin. It was also examined whether the order of saturating the resin with the two cations had any effect on their exchangeability.

## EXPERIMENTAL

"Zeo-Karb 225" was employed as the cation-exchange resin. The nature of the resin and the methods for its regeneration and purification have been described previously (Pochhali, this *Journal*, 1960, **37,** 451). For determining the total exchange capacity, a weighed quantity of the regenerated, air-dried resin was allowed to react with a standard alkali, added in excess, in a Jena glass bottle by shaking in a mechanical shaker for half an hour, and then the unchanged alkali was titrated against a standard acid. The amount of alkali consumed in reaction with the resin in its H-form gave the total exchange capacity expressed in m.e/g. of the air-dried resin.

The following different heteroionic resins were prepared :

$$\left.\begin{matrix} NH_4 \\ K \end{matrix}\right\}\text{—resin,} \qquad \left.\begin{matrix} Ca \\ NH_4 \end{matrix}\right\}\text{—resin and} \qquad \left.\begin{matrix} Ba \\ Ca \end{matrix}\right\}\text{—resin.}$$

The exchanger was saturated with the two kinds of ions at three different mutual degrees of saturation, e.g., 25-75, 50-50 and 75-25%. The actual experiment was arranged

in the following way: A weighed amount (~ 1 g.) of the H-form of the resin was taken in a Jena glass bottle. A calculated amount of the first cation was introduced into the resin by adding its hydroxide solution to the resin and keeping the mixture for 24 hours with occasional shaking. The second cation was then introduced similarly by adding the calculated amount of the corresponding hydroxide solution, so that the resin taken would now become completely saturated with the two cations added. The mixture was again kept for 24 hours with occasional shaking in a mechanical shaker. Then after decanting the clear supernatant liquid, which was almost neutral, the resin was partially dried in air in the bottle at room temperature. A second set of resin salts was prepared by reversing the order of introduction of the two cations. To distinguish between the two sets, these were represented in two different ways, e.g., A-B-R and B-A-R. As for example, $NH_4$-K-R would mean the resin salt which was prepared by introducing $K^+$ first and then $NH_4^+$, whereas K-$NH_4$-R would represent the resin salt in which $NH_4^+$ was introduced first and then $K^+$.

To the heteroionic resin salts in bottles were added NaCl solutions in such quantities as contained amounts of $Na^+$ exactly equivalent to the amounts of the total exchangeable cations present in the resins. The volume of the solution was always kept fixed at 50 c.c. The systems were then allowed to attain equilibrium on keeping for 24 hours with occasional shaking in a mechanical shaker. After equilibrium the clear solutions were analysed for estimation of the two cations replaced from the resins. The usual analytical methods were employed as described in an earlier publication (*loc. cit.*).

## DISCUSSION

The results of the replacement experiments are presented graphically in Figs. 1, 2 and 3 for the

$$\left.\begin{matrix} K \\ NH_4 \end{matrix}\right\}\text{—resin,}\quad \left.\begin{matrix} Ca \\ NH_4 \end{matrix}\right\}\text{—resin and}\quad \left.\begin{matrix} Ba \\ Ca \end{matrix}\right\}\text{—resin}$$

respectively. It is observed that the symmetry values of the different pure forms of the resin against a particular cation, e.g., $Na^+$, are as shown in Table I.

FIG 1

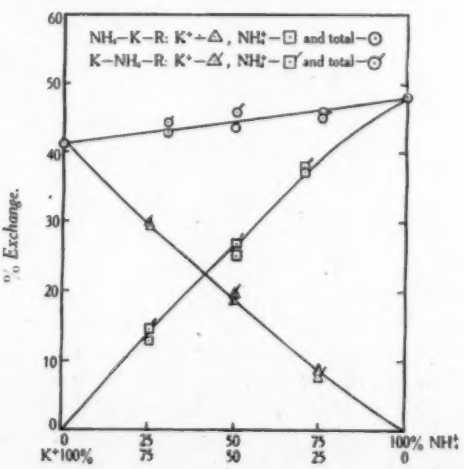


TABLE I

| Resin salt. | Symmetry value. | Resin salt. | Symmetry value. |
|---|---|---|---|
| $NH_4$-resin | 48.0 | Ca-resin | 13.9 |
| K-resin | 41.0 | Ba-resin | 8.8 |

The order of ease of release for the different cations from their corresponding pure resin salts is: $NH_4^+ > K^+ > Ca^{2+} > Ba^{2+}$.

Now, if we focus our attention to the percentage exchange of the ions from the mixed resins, it is found that the release of the ion having higher release capacity is enhanced and that of the ion having lower release capacity is suppressed. This interaction, e.g., the enhancement in the release of one ion at the expense of that of the second ion, is somewhat proportional to the ratio of their ease of release, *i.e.*, their symmetry values. Thus the interaction is greatest in the case of $Ca-NH_4$ resin and least in the system $K-NH_4$ resin. On comparing the symmetry values the ratio of $NH_4^+$ to $Ca^{2+}$ is also found to be highest, being 48.0 : 13.9, but the ratio of those between $NH_4^+$ and $K^+$ is very small, being only 48.0 : 41.0. The ratio of the symmetry values of $Ca^{2+}$ and $Ba^{2+}$ (13.9 : 8.8) being intermediate between the above two, the interaction also lies in between them.

But though the release of one ion is enhanced and that of the other is suppressed, the total percentage of exchange from the resins with different degrees of saturation with respect to the two cations comes out to be purely additive; neither antagonism nor superadditivity is found as is evident from the straight line curves for the total exchange.

FIG. 2

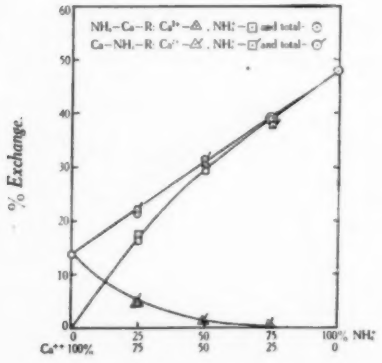
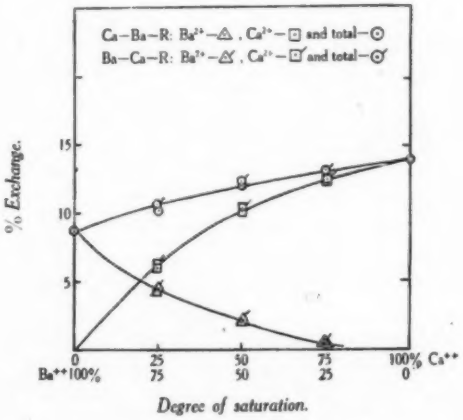


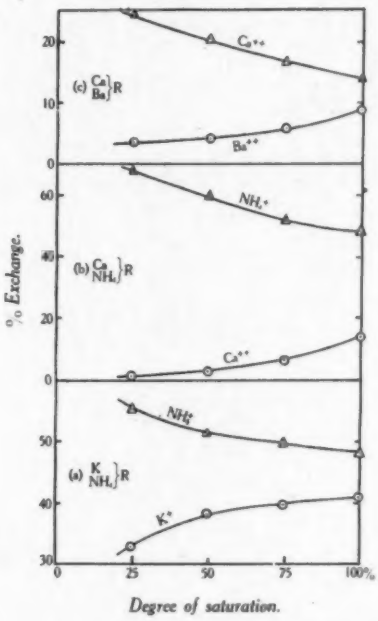

FIG. 3




From the percentage exchange of the two ions from the two different sets of the heteroionic resin salts, A-B-R and B-A-R, it becomes quite clear that unlike some clay minerals, the order of introduction of the two ions into the resin has no effect on their replacement. From both the series of mixed resins, A-B-R and B-A-R, the exchange of $A^+$ or $B^+$ from each of them is the same, within the experimental error, at the corresponding degrees of saturation. The effect observed in clay minerals is explained on the basis that all the exchange sites in them are not identical; some exchange sites are of higher binding energy than that of others. But here in the case

of this resin we may infer that all the exchange sites are identical ; there is no distinction between them with respect to binding energy.

FIG. 4




The variation in the percentage release of the two complementary ions with their degrees of saturation in the resin is shown in Fig. 4. Here the quantity of individual ion replaced has been calculated as the percentage of the amount of that particular ion present originally in the resin instead of that of the total amount of cations in the resin, as has been plotted in Figs. 1-3. It clearly shows how the replacement of a particular ion varies with its degree of saturation in the resin as well as on the nature of the complementary ion.

It is observed from the curves that in the system $K—NH_4—R$, the release of $K^+$ increases with its degree of saturation whereas the release of $NH_4^+$ decreases as its degree of saturation is increased. It is also seen that the replacement of $NH_4^+$ is enhanced and that of $K^+$ is suppressed in presence of the other, and this interaction increases with the degree of saturation of the complementary ion. In the system, $Ca—NH_4—R$, the relation between release and degree of saturation for $Ca^{2+}$ and $NH_4^+$ is similar to that for $K^+$ and $NH_4^+$ except for the fact that the mutual interaction is far more intense, as is to be expected from the large difference between the symmetry values of $Ca^{2+}$ and $NH_4^+$. The replacement of $Ca^{2+}$ is depressed to a large extent with increasing degree of saturation with $NH_4^+$. But in the system $Ba—Ca—R$, the release of $Ca^{2+}$ is enhanced instead of being depressed and that of $Ba^{2+}$ is suppressed as $Ca^{2+}$ is more replaceable than $Ba^{2+}$.

So it may be generalised that the release of the more replaceable ion is enhanced and that of the less replaceable ion is depressed in presence of the other, and this mutual interaction increases with the degree of saturation of the complementary ion.

How the selectivity coefficient of $Na^+$ against the other two ions present in the resin varies with their degrees of saturation is shown below. This selectivity coefficient can be represented as:

$$K^{Na}_{A+B} = \frac{\left[\frac{Na}{A+B}\right]_R}{\left[\frac{Na}{A+B}\right]_S}$$

where Na, A and B within parentheses represent the equivalents of $Na^+$, $A^+$ and $B^+$, the subscripts R and S indicating the resin and solution phase respectively. Here the concentration of the added $Na^+$ was always kept constant at the symmetry concentration. Hence the variation in the selectivity coefficient with the degree of saturation with respect to the two ions A and B present in the resin can be well compared. Since with the two series of resin salts, A-B-R and B-A-R, the values of the selectivity coefficients differ very slightly, the mean of the two values has been shown.

TABLE II

*Values of* $K^{Na}_{A+B}$.

| Resin salt | | Degree of saturation | | | | |
|---|---|---|---|---|---|---|
| | A: | 100 | 75 | 50 | 25 | 0 |
| A, B } R | B: | 0 | 25 | 50 | 75 | 100 |
| K, $NH_4$ } –R | | 0.48 | 0.60 | 0.67 | 0.71 | 0.85 |
| Ca, $NH_4$ } –R | | 0.026 | 0.078 | 0.21 | 0.41 | 0.85 |
| Ba, Ca } –R | | 0.009 | 0.014 | 0.020 | 0.025 | 0.026 |

From the data in Table II the values of the selectivity coefficient appear gradually to increase from pure A-resin to pure B-resin with increasing degree of saturation with B, A and B being the less replaceable and more replaceable ion respectively within the heteroionic resin.

The author takes this opportunity to express his grateful thanks to Prof. S. N. Mukherjee, D.Sc., Professor of Physical Chemistry, Jadavpur University and to Prof. S. K. Mukherjee, D.Sc., Unesco Consultant, Universitas Sumatra, Utera, Indonesia, for their kind and helpful suggestions and discussion.

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# ION-EXCHANGE REACTIONS WITH HETEROIONIC SYNTHETIC RESINS. PART II. ANION EXCHANGE

By L. Pochhali

Ion-exchange reactions with an anion-exchange resin, saturated with two different types of anions at different degrees of saturation, against a third anion have been studied by equilibrium method. Exchange of the more replaceable ion appears to increase and the less replaceable ion is suppressed; the interaction goes on increasing with the degree of saturation of the complementary ion. Of the three anions studied: $Cl^-$, $NO_3^-$ and $SO_4^{2-}$, when one of the saturating ions is $SO_4^{2-}$, the total exchange comes out to be antagonistic. The order of introduction of the $SO_4^{2-}$ affects its release, showing that when it is introduced first it can take up exchange sites of higher binding energy. The structure of the strong base-anion exchange resin of polyammine type differs from that of sulphonated polystyrene resin, a strong acid cation exchanger.

In Part I (Pochhali, this *issue*, p. 521) the complications of ion-exchange reactions with heteroionic ion exchangers have been discussed. This present work deals with exchange reactions with an anion-exchange synthetic resin. It is mainly concerned with the study of the effect of the degree of saturation on the exchangeability of an anion from an anion-exchange resin, saturated with two different types of anions. The ions were exchanged by a third anion added at its symmetry concentration. Influence of the order of saturating the resin with the two anions on their exchangeability has been examined.

## Experimental

As the anion exchanger, 'De-Acidite FF', a strong base synthetic resin, was used for the study. The nature of this resin and the method for its regeneration and purification have been described in an earlier publication (Pochhali, this *Journal*, 1960, **37** 451).

The total ion-exchange capacity of the resin was determined in the following manner. A weighed quantity (3-4 g.) of the air-dried resin in the hydroxyl form was taken in a column and washed with distilled water till the effluent became colorless with phenolphthalein. A 5% solution of $Na_2SO_4$ was passed through the column and the effluent was collected in a litre volumetric flask up to the mark. The collected solution (100 c.c.) was titrated against a standard $H_2SO_4$ solution. The exchange capacity in m.e./g. of the air-dried resin was calculated from the titration value.

From the hydroxyl form of the resin, the following heteroionic resin salts were prepared:

$$R\begin{cases}Cl\\NO_3\end{cases},\quad R\begin{cases}Cl\\SO_4\end{cases}\quad \text{and}\quad R\begin{cases}NO_3\\SO_4\end{cases}$$

The resin was saturated with the two types of anions at three different mutual degrees of saturation: 25-75, 50-50 and 75-25%. A weighed amount (~1 g.) of the OH-form of the resin was taken in a Jena glass bottle. A calculated amount of the first anion was introduced into the resin by adding its acid solution (HCl, $HNO_3$ or $H_2SO_4$) and keeping the mixture for 48 hours with occasional shaking. The second anion was then introduced similarly by adding the calculated volume of the corresponding standard acid solution so that the resin taken would now become completely saturated with the two anions. The mixture was again kept for 48 hours with occasional shaking in a mechanical shaker. The clear, practically neutral supernatant liquid was decanted and the resin was partially dried in air in the bottle at room temperature. A second set of resin salts was prepared by reversing the order of introduction of the two anions. To distinguish between the

two sets, we represent these as R-A-B and R-B-A; e.g. R-Cl-$NO_3$ represents the resin which is neutralised first with HCl and then with $HNO_3$ whereas R-$NO_3$-Cl represents the resin salt which is prepared by adding first $HNO_3$ and then HCl.

To these resin salts in bottles was added NaOH solution containing $OH^-$ exactly equivalent to the amounts of the total exchangeable anions originally present in the resins. The total volumes of the solutions were kept constant at 50 c.c. The systems were then allowed to equilibrate on keeping for 48 hours with occasional shaking in a mechanical shaker. After equilibrium the clear solutions were analysed for estimating the two anions replaced.

The chloride was estimated volumetrically with a standard $AgNO_3$ solution using fluorescein as indicator, the nitrate by the modified Kjeldahl method using Devarda's alloy for reduction, and the sulphate gravimetrically as $BaSO_4$.

## DISCUSSION

The results of the exchange experiments are shown graphically in Figs. 1-3. Here the amounts of each anion replaced are expressed as percentages of the total amount of anions originally present in the resins.

FIG. 1

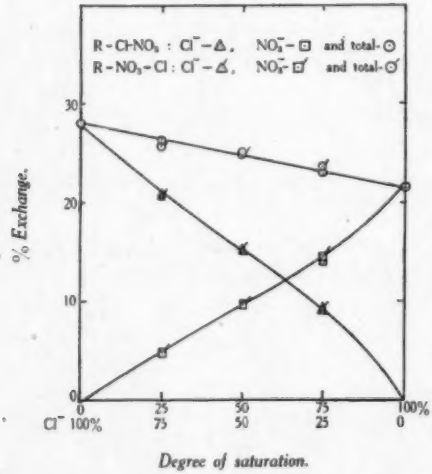
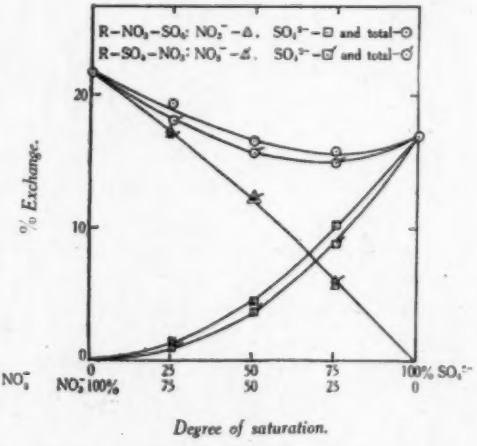



FIG. 2



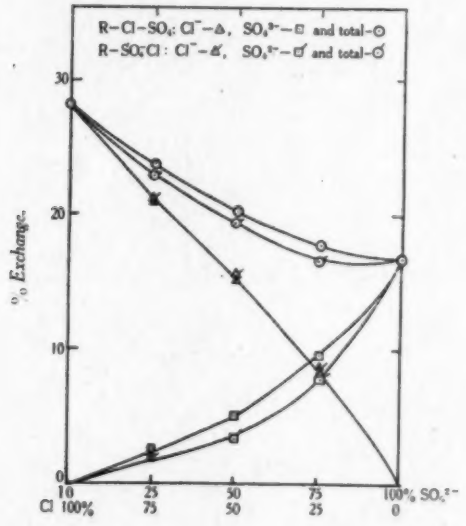

From the replacement data of the anions from their pure forms of the resin against the same anion, $OH^-$, the symmetry values are found to be as Cl-resin, 28.3; $NO_3$-resin, 21.6; $SO_4$-resin 16.7.

A comparison of the amounts of release for a particular anion from the two series of resin salts, e.g., R-A-B- and R-B-A, shows no difference between R-Cl-$NO_3$ and R-$NO_3$-Cl; the release of $SO_4^{2-}$ from the salts in which it is introduced first is, however, slightly less than that where it was introduced last. This is true of Cl-$SO_4$ and $NO_3$-$SO_4$ series. The order of saturating the resin with $SO_4^{2-}$ thus appears to affect its exchangeability. The $SO_4^{2-}$ ion is held more strongly when it is introduced first.

The results for the total amount of anions replaced from the heteroionic resin salts at different degrees of saturation with respect to the two anions point to the fact that while in the Cl-$NO_3$

series, it is purely additive, in the Cl-$SO_4$ and $NO_3$-$SO_4$ series, the total amount of exchange is certainly antagonistic. In the Cl-$NO_3$ systems, though the $Cl^-$ ion slightly suppresses the release of $NO_3^-$, its own release is enhanced slightly so that the resulant effect becomes additive. But in the case of Cl-$SO_4$ and $NO_3$-$SO_4$ systems, both $Cl^-$ and $NO_3^-$ suppress the release of $SO_4^{2-}$ to such an extent that the total amount of anions replaced from their corresponding resin salts falls short of that demanded by additive behaviour, and hence antagonism is observed.

FIG. 3




The quantity of release of an individual anion is shown in Fig. 4 as the percentage of the amount of that particular ion present in the resin, instead of the total amounts of anions in the resin.

As in the case of heteroionic cation exchanger, here also a similar trend is observed in the percentage release with respect to the degree of saturation. The release of the more replaceable anion increases with its falling degree of saturation, but that of the less replaceable ion increases with its increasing degree of saturation. Thus in the Cl-$NO_3$ series, the replacement of $Cl^-$ increases as its degree of saturation decreases, but that of $NO_3^-$ decreases with its decreasing degree of saturation. But in the $NO_3$-$SO_4$ systems, $NO_3^-$ behaves in the opposite way. With falling degree of saturation, the release of $NO_3^-$ increases whereas that of $SO_4^{2-}$ decreases. The same is the case with the Cl-$SO_4$ series.

Similar to the case of cation exchange from heteroionic systems, the exchange of the more exchangeable anion is also enhanced and that of the less exchangeable ion is suppressed in presence of each other. This mutual interionic effect is greater in the $NO_3$-$SO_4$ systems than in the Cl-$SO_4$ systems. At corresponding degree of saturation $NO_3^-$ suppresses more effectively the release of $SO_4^{2-}$ than the $Cl^-$ ion.

The variation of the selectivity coefficient of $OH^-$ against the other two anions present in the resin ($K_{A+B}^{OH^-}$) with their degrees of saturation is shown in Fig. 5. As with the resin salts,

R-A-B and R-B-A, the values of the selectivity coefficient differ very slightly, the mean of the two values has been taken.

FIG. 4

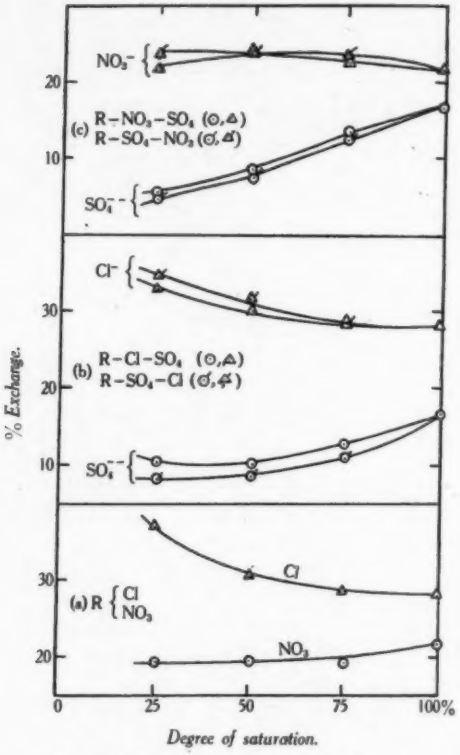
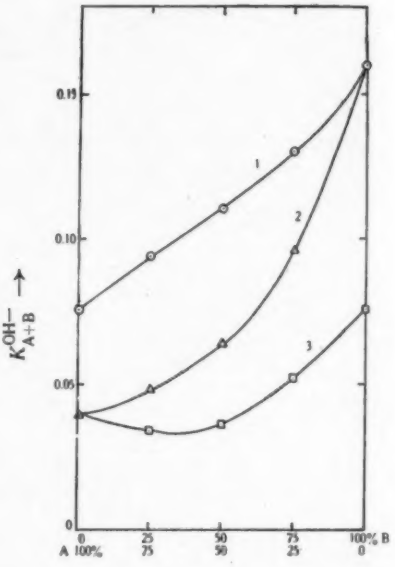



FIG. 5




| A. | B. | Curve. |
|---|---|---|
| $NO_3^-$ | $Cl^-$ | 1 |
| $SO_4^{2-}$ | $Cl^-$ | 2 |
| $SO_4^{2-}$ | $NO_3^-$ | 3 |

The variation in the values of the selectivity coefficient with the degree of saturation is found to be gradual in R-Cl-$NO_3$ like the cation-exchange resin, 'Zeo Karb 225' (this *issue*, p. 521). But where one of the saturating ions is $SO_4^{2-}$, $K^{OH^-}_{A+B}$ has a tendency of having a minimum value at a certain degree of saturation, which is actually realised in the case of R-$NO_3$-$SO_4$. This also shows that $SO_4^{2-}$ can enter positions of higher binding energy in the exchange resin and is released with more difficulty than monovalent anions like $Cl^-$ and $NO_3^-$.

The observations recorded here indicate that the structure of the polyammine resins like 'De-Acedite FF' differs from that of the cation-exchange resins like 'Zeo-Karb 225'. In the latter all the exchange sites are identical whereas in this anion-exchange resin there are some exchange sites, which are quite different from others regarding their binding energy for ions.

The author's grateful thanks are due to Prof. S. N. Mukherjee, D.Sc., Head of the Department of Chemistry, Jadavpur University and to Prof. S. K. Mukherjee, D.Sc., Unesco Consultant, Universitas Sumatra, Utara, Indonesia, for their kind and helpful suggestions and encouragement.

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# PREPARATION AND STUDY OF HYDROXYTRIAZINES AS ANALYTICAL REAGENTS. PART II. 3-HYDROXY-1-*p*-TOLYL-3-PHENYLTRIAZINE AS A REAGENT FOR PALLADIUM AND COPPER

By H. K. L. Gupta, T. C. Jain and N. C. Sogani

Out of five hydroxytriazines studied as analytical reagents, 3-hydroxy-1-*p*-tolyl-3-phenyltriazine is found to be a highly selective reagent for the gravimetric estimation of copper and palladium and their separation from a large number of elements by direct weighing. The *p*H range for quantitative precipitation is from 2.0 to 7.0 and 1.6 to 7.0 respectively with only a slight excess of the reagent. *p*H between 2.0 and 3.0 is found to be the most suitable as it facilitates the hydrolysis of excess of the reagent and increases specificity. The complexes are stable towards heat and acid and are very granular.

In Part I of this series (Sogani and Bhattacharyya, this *Journal*, 1959, **36**, 563) a general method of preparing hydroxytriazines and their precipitating characteristics were reported. The present communication describes the study of analytical usefulness of five more compounds. Out of these, 3-hydroxy-1-*p*-tolyl-3-phenyltriazine has been examined in detail. It offers an advantage that excess of the reagent can be removed easily by heating the weakly acidic reaction medium whereby it is completely hydrolysed into water-soluble products.

Below *p*H 3.0 it forms complexes only with $Cu^{2+}$, $Pd^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $V^{3+}$, $Ti^{4+}$, vanadate and molybdate. The complexes given by $Cu^{2+}$ and $Pd^{2+}$ are not decomposed on heating in acidic medium, thus making it a highly specific reagent for the gravimetric determination of these elements by direct weighing and their separation from $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Bi^{3+}$, $Sb^{3+}$, $As^{3+}$, $Hg^{2+}$, $Pt^{4+}$, $Zr^{4+}$, $Ce^{4+}$, $Th^{4+}$, $UO_2^{2+}$, tungstate, phosphate, fluoride,alkali and alkaline earth metals and by use of proper masking agents from $Fe^{2+}$, $Fe^{3+}$, $Sn^{4+}$, $Ti^{4+}$, and molybdate. The composition of the complexes correspond to $(C_{13}H_{12}ON_3)_2$ M, where M=copper or palladium, and can be represented as shown in Part I (*loc. cit.*).

## Experimental

The compounds were prepared by the method described in the earlier communication (*loc. cit.*). Table I summarises the physical properties of these compounds.

Slightly modified method was used for the preparation of 3-hydroxy-1-*o*-carboxyphenyl-3-phenyltriazine. The compound after precipitation was immediately filtered under suction. It was dissolved in minimum quantity of ethanol and filtered. It was reprecipitated by adding a small amount of water. It was again dissolved in minimum quantity of ethanol and kept in a refrigerator overnight when white needle shaped crystals separated.

Table I

| Compound. $C_6H_5$-N(OH)N=N-R where R- = | Cryst. from | M. P. | Cryst. shape. | % Nitrogen. Found. | Calc. |
|---|---|---|---|---|---|
| I. $-C_6H_4CH_3$ (*p*) | 95% Ethanol | *130° | Greenish yellow needles | 18.81 | 18.50 |
| II. $-C_6H_4Br$ (*p*) | Do | †154° | Deep green shining needles | 14.08 | 14.38 |
| III. $-C_6H_4COOH$ (*o*) | Very small vol. of alc. | 35° | White needles | 16.47 | 16.15 |
| IV. $-C_6H_4CO.CH_3$ (*p*) | 95% Ethanol | 154° | Light green flakes | 16.23 | 16.47 |
| V. $-C_6H_4NH.CO.CH_3$ (*p*) | Do | 146.5° | Do | 20.58 | 20.74 |

* Lit. M.P. 130° (Bamberger and Busdorf, *Ber.*, 1900, **33**, 3510), and 131° (Elkins and Hunter, *J. Chem. Soc.*, 1938, 1346).
† Lit. M.P. 154.5° (Bamberger, *Annalen*, 1918, **420**, 164).

The general precipitating properties, and colour and nature of complexes formed by these compounds resemble essentially the parent compound (*loc. cit.*). Precipitates formed by *o*-carboxy derivative (III) are gelatinous in nature, unstable towards heat, and unsuitable for analytical purposes. Complexes given by *para*-bromo (II) and tolyl (I) derivatives are more stable towards heat and acid than the parent compound.

*Hydrolysability of the Compounds.*—Hydroxytriazines hydrolyse on heating in weakly acidic medium, but only some of them hydrolyse to yield water-soluble products. This is an important property which imparts a compound all the advantages of a water-soluble reagent. Any excess of the reagent present in the reaction medium on heating during the normal processing of the complex, if it hydrolyses into water-soluble products, can easily be eliminated by simple washing. The absence of hydrolysed products in the wash water can readily be ascertained by testing with a drop of dilute NaOH solution.

Experiments were conducted to study the hydrolysis of these compounds. Distilled water (150 c.c.), 10% HCl (v/v., 2 c.c.) and 1% ethanolic solution of the compound were taken in a r.b. flask fitted with an air condenser. It was kept on a boiling water bath for about 45 minutes and was occasionally shaken. Complete disappearance of solid matter from the medium indicated complete hydrolysis of the compound into water-soluble products. It was further verified by taking out a drop of the liquid from the flask and testing it with dilute NaOH solution on a spot plate. Unhydrolysed hydroxytriazine shows an intense yellow colour, hydrolysed products give bluish black colour, and incomplete hydrolysis is indicated by a greenish yellow or greenish blue colour, depending on the extent of reaction. The mechanism of hydrolysis has already been reported earlier (*loc. cit.*).

A standard solution was prepared by dissolving palladium chloride (1 g.) in HCl (conc., 5 c.c.) and the solution diluted to one litre. Its palladium content was determined by using dimethylglyoxime. $CuSO_4$, $5H_2O$ (1.8380 g.) (A. R.) was dissolved in distilled water and made to one litre. The amount of copper in the solution was determined by standard methods. In special cases where sulphate ion interfered, copper acetate was used. 1% Solutions (w/v) of reagent grade soluble salts of various metals were used for quantitative separations.

Normal hydrochloric acid, sodium acetate (10%, w/v), and 10% sodium potassium tartrate solutions were used for adjustment of *p*H.

A Beckman *p*H meter, Model H-2, was used for *p*H measurements, Mettler's single pan balance for weighing, and sintered crucible No. 3 for collecting the precipitates. Ashless filter paper No. 40 was employed for general filtration.

*Properties of Complexes.*—The palladium complex is yellowish brown in colour, readily soluble in chloroform and benzene, and fairly soluble in ether and acetone. It is only slightly soluble in ethanol. It was crystallised from acetone, m.p. 258°. It is stable towards heat and moderate concentrations of acids and can be safely heated from 120° to 130° to a constant weight in about half an hour. [Found (micro): N, 7.60. $(C_{13}H_{12}ON_3)_2Pd$ requires N, 7.51%].

The copper complex is chocolate-brown in colour. As regards stability towards heat and acid and solubility in organic solvents, it resembles palladium complex. It was crystallised from acetone, m.p. 195-96°; lit. 191° (Elkins and Hunter, *loc. cit.*). [Found : N, 8.34. $(C_{13}H_{12}N_3O)_2Cu$ requires N, 8.14%].

*Conditions for Quantitative Precipitation.*—Various determinations were done using varying amounts of the reagent under different *p*H conditions. It was found that palladium and copper were

completely precipitated between *p*H 1.6 and 7.0, and *p*H 2.0 and 7.0 respectively with only 15 to 20% excess of the reagent. We have, however, carried out the estimations between *p*H 2.0 and 3.0 as it increased the specificity of the reagent and facilitated removal of the excess reagent by hydrolysis. The precipitates formed under these conditions are very granular.

### *Procedure for Palladium*

A solution of palladium containing 10 to 20 mg. of the metal is diluted to about 120 c.c. 10% Sodium acetate or sodium potassium tartrate (w/v, 2-3 c.c.) and *N*-HCl (2 c.c.) are added to it so as to bring *p*H of the solution at 2.0-3.0. It is warmed and 1% ethanolic solution of the reagent (about 20 % excess) is added with constant stirring. Palladium complex separates as a dirty green precipitate. It is heated on a boiling water bath for about an hour, during which period the precipitate changes its colour to yellowish brown and becomes granular. The supernatant liquid also becomes clear. It is filtered hot through a weighed sintered glass crucible No. 3, washed with hot water 3 to 4 times till the washings do not give bluish violet colour with a drop of NaOH solution. The complex is dried to a constant weight at 120-30°. It takes about half an hour. The weight of the complex multiplied by the conversion factor, 0.1909, gives the weight of palladium. The results are recorded in Table II.

TABLE II

| Pd taken. | Foreign ion. | Pd complex. | Pd found. | Error. | Pd taken. | Foreign ion. | | Pd complex. | Pd found. | Error. |
|---|---|---|---|---|---|---|---|---|---|---|
| 20.64 mg. | .. | 0.1084 g. | 20.69 mg. | +0.05 mg. | 13.76 | $Ti^{4+}$, | 0.05 | 0.0723 | 13.80 | +0.04 mg. |
| 13.76 | .. | 0.0720 | 13.74 | −0.02 | 13.76 | $Bi^{3+}$, | 0.05 | 0.0722 | 13.78 | +0.02 |
| 6.88 | .. | 0.0362 | 6.91 | +0.03 | 13.76 | $Sb^{3+}$, | 0.05 | 0.0723 | 13.80 | +0.04 |
| 20.64 | $Co^{2+}$, 0.05 g. | 0.1083 | 20.67 | +0.03 | 13.76 | $Pt^{4+}$, | 0.05 | 0.0720 | 13.74 | −0.02 |
| 20.64 | $Ni^{2+}$, 0.05 | 0.1082 | 20.65 | +0.01 | 20.64 | $Sn^{4+}$, | 0.05 | 0.1084 | 20.69 | +0.05 |
| 20.64 | $Mn^{2+}$,0.05 | 0.1084 | 20.69 | +0.05 | 20.64 | $Ce^{4+}$, | 0.05 | 0.1082 | 20.65 | +0.01 |
| 20.64 | $Zn^{2+}$, 0.05 | 0.1080 | 20.64 | 0.00 | 20.64 | $Zr^{4+}$, | 0.05 | 0.1083 | 20.67 | +0.03 |
| 20.64 | $Cd^{2+}$, 0.05 | 0.1081 | 20.63 | −0.01 | 20.64 | $MoO_4^{2-}$, | 0.05 | 0.1081 | 20.63 | −0.01 |
| 13.76 | $Fe^{2+}$, 0.05 | 0.0718 | 13.70 | −0.06 | 20.64 | $PO_4^{3-}$, | 0.10 | 0.1082 | 20.65 | +0.01 |
| 13.76 | $Fe^{3+}$, 0.05 | 0.0722 | 13.78 | +0.02 | 20.64 | $F^-$, | 0.10 | 0.1084 | 20.69 | +0.05 |

The interference due to $Fe^{2+}$, $Fe^{3+}$, $Ti^{4+}$, and molybdate was eliminated by adding 0.5 g. of sodium fluoride as a masking agent. The hydrolysis of $Sn^{4+}$ and $Zr^{4+}$ was also prevented as given above, and that of $Ce^{4+}$ by adding a small amount of solid ammonium sulphate. In case of $Bi^{3+}$ and $Sb^{3+}$ sodium potassium tartrate was used as a buffering agent.

### *Procedure for Copper*

The procedure adopted for determining copper is the same as given above. The weight of copper complex multiplied by 0.1232 gives the weight of copper. Table III records the results obtained.

The properties and stabilities of palladium and copper complexes are very similar. Hence observations recorded in case of palladium in presence of foreign ions are also applicable in the case of copper. For the sake of brevity all these have not been included here.

TABLE III

Cu taken = 11.71 mg.

| Foreign ion. | | Cu complex. | Cu found. | Error. | Foreign ion. | | Cu complex. | Cu found. | Error. |
|---|---|---|---|---|---|---|---|---|---|
| .. | | 0.0949 g. | 11.69 mg. | −0.02 mg. | $Cd^{2+}$, | 0.05 | 0.0949 | 11.69 | −0.02 |
| $Co^{2+}$, | 0.05 g. | 0.0953 | 11.74 | +0.03 | $Fe^{2+}$, | 0.05 | 0.0953 | 11.74 | +0.03 |
| $Ni^{2+}$, | 0.05 | 0.0950 | 11.70 | −0.01 | $Fe^{3+}$, | 0.05 | 0.0955 | 11.76 | +0.05 |
| $Zn^{2+}$, | 0.05 | 0.0947 | 11.66 | −0.05 | $Cr^{3+}$, | 0.05 | 0.0947 | 11.66 | −0.05 |
| $Mn^{2+}$, | 0.05 | 0.0952 | 11.72 | +0.01 | $Al^{3+}$, | 0.05 | 0.0955 | 11.76 | +0.05 |

3-Hydroxy-1-*p*-tolyl-3-phenyltriazine is a better reagent than the parent compound in that the reagent as well as the complexes given by it are more stable and the conversion factors more favourable.

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# STUDIES IN TERPENES. PART VIII. BROMINE DEHYDROGENATION OF SOME TERPENOIDS

By James Verghese

That Baeyer-Villiger method of bromine dehydrogenation is based on false premises, there is no need to prepare 'fully' brominated derivatives, and it is incomplete bromination which offers a guarantee to successful aromatisation by heat and alkali have been substantiated by the aromatisation of 3-carene, α-pinene, terpinolene, and terpineol. Moreover, with bromine 3-carene furnishes *p*-and *m*-cymenes, and α-pinene, *p*- and *o*- cymenes. These two-way aromatisations are novel reactions in terpene chemistry.

Terpenoid bromides have been decomposed to *p*-cymene by heat (Wallach and Berthold, *Nachr. kgl. Ges. Gottingen*, 1915; Wallach, *Annalen*, 1918, **414,** 206), by alkali (Wallach, *ibid.*, 1895, **287,** 383), and by stepwise reduction ("the exhaustive bromination method") (Baeyer and Villiger, *Ber.*, 1898, **31,** 1401). Examples are the formation of *p*-cymene from α-terpineol dibromide by heating (Wallach *et al.*, *loc. cit.*), α-phellandrene dibromide under the influence of alkali (Wallach, *loc. cit.*), and limonene perbromide by stepwise reduction (Baeyer and Villiger, *loc. cit.*). Of these, the most important but little investigated are the thermal and alkali decomposition techniques. Known long ago, these techniques rest on the fact that under certain conditions bromine affords with terpenoids, at relatively low temperatures, high boiling products, which being heat and alkali labile, can be broken down to benzenoid counterparts without reduction (cf. Olsen, *Ber.*, 1948, **81,** 131). Thus, the transformation of limonene to *p*-cymene effected *via* the perbromide, $C_{10}H_{13}Br_7$ (Baeyer and Villiger, *loc. cit.*), can be better accomplished by heating the tetrabromide, $C_{10}H_{16}Br_4$ (Olsen, *loc. cit.*); spontaneous cleavage of three moles of hydrogen bromide from the perbromide still leaves four atoms of bromine, which can only be expelled by reduction (Olsen, *loc. cit.*). From this and other conversions it is concluded that (*i*) the Baeyer-Villiger dehydrogenation method is based on false premises, (*ii*) there is no need to prepare 'fully' brominated derivatives, and (*iii*) it is incomplete bromination which offers a guarantee to successful aromatisation by heat and alkali (cf. Olsen, *loc. cit.*). A study was therefore undertaken on the bromine dehydrogenation of 3-carene, α-pinene, terpinolene, and terpineol to gain further confirmation of this conclusion, and also to demonstrate the two-way opening of the bicyclic terpenes leading to a mixture of cymenes.

## Experimental

3-Carene, isolated by a two-fold fractionation of Indian turpentine oil of *Pinus longifolia* (Roxb) (Bareilly First Quality), has the following properties: b.p. 170-71°/760mm, $n_D^{20}$ 1.4728, $d_4^{20}$ 0.8614. Nitrosate, prepared from this oil, after recrystallisation from chloroform by addition of cold methanol melted at 147° (decomp.) (lit. 147.5°; Simonsen, *J. Chem. Soc.*, 1920, **117,** 574).

α -Pinene was obtained by fractionation of a sample, kindly supplied by Hercules Powder Company, Wilmington, U.S.A., and has b.p. 156°/760mm, $n_D^{20}$ 1.4657 and $d_4^{20}$ 0.8592.

Terpinolene tetrabromide was prepared as follows. Cold bromine was added dropwise to terpinolene (b.p. 184-86°/760mm, $n_D^{20}$ 1.4865) which had been dissolved in a mixture of amyl alcohol and diethyl ether (1:2) and cooled in a freezing mixture until coloured. The tetrabromide was precipitated with cold methanol. Solids separated were thrice precipitated from

chloroform with methanol. Crystals thus obtained melted at 116°; m.p. remained undepressed by an admixture with an authentic sample of terpinolene tetrabromide. Terpineol has b.p. 218-19°/760mm, $n_D^{20}$ 1.4829 and $d_4^{20}$ 0.9332.

*Dehydrogenations*

*3-Carene.*—To cooled 3-carene (21.25g., 0.1562*M*) in a freezing mixture cold bromine (24.96g., 0.1562*M*) was added dropwise with occasional shaking. Addition of bromine was attended with very slight formation of hydrogen bromide. The reaction mixture was refluxed for 24 hours with copious evolution of HBr. The reaction mixture was then washed with 10% NaOH solution and steam-distilled (yield 15.2g.). The volatile portion was shaken with twice its volume of cold 80% $H_2SO_4$. Saturates thus obtained were separated in the usual manner and carefully fractionated to yield a cut (5.6g.), b.p. 170-80°/760mm, $n_D^{20}$ 1.4886 and $d_{30}^{30}$ 0.8592.

This oil (480mg.) was oxidised with potassium dichromate-sulphuric acid mixture (Leo *et al.*, *Curr. Sci.*, 1953, **22,** 112; *Bull. Nat. Inst. Sci., India*, 1959, No.12, 179). Total terephthalic and isophthalic acids amounted to 380mg. These were separated from each other as barium salts (Smith, *J.Amer. Chem. Soc.*, 1921, **43,** 1921) (terephthalic acid: yield 270mg., dimethyl ester, m.p. 141°; isophthalic acid: yield 80mg., dimethyl ester, m.p. 65°).

*α -Pinene.*—On treatment with bromine (24.96g., 0.1562M) in a manner analogous to that of 3-carene, α -pinene (21.25g., 0.1562*M*) afforded saturates (*ca.* 3.5g., with b.p. 168-76°/760mm, $n_D^{30}$ 1.4889). Oxidation of 500mg. of this oil with potassium dichromate — sulphuric acid mixture (Leo *et al.*, *loc. cit.*) and alkaline potassium permanganate gave respectively *ca.* 250mg. of terephthalic acid (nitro derivative, m. p. 269°; Lange *et al.*, *J. Chem. Ed.*, 1955, **32,** 40) and *ca.* 80mg. of *o*-phthalic acid (phthalanil, m.p. 270°).

*Terpinolene.*—Terpinolene tetrabromide (12g.) was heated under reflux for 1 hour, and then distilled (yield *ca.* 2g.). The distillate was treated with cold 80% $H_2SO_4$, and the saturates thus obtained were oxidised with potassium permanganate (Wallach, *Annalen*, 1891, **264,** 10; Solodskii, *Lesokhim Prom.*, 1940, **3,** *iv*, 8) to furnish *p*- (α-hydroxypropyl[i]) -benzoic acid, m.p. 156°; mixed with an authentic sample of the acid, there was no depression in m.p.

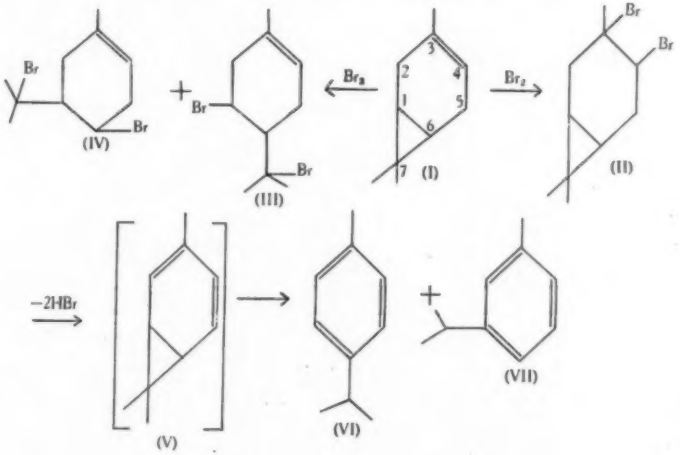
*Terpineol.*—To terpineol (20g., 0.1297*M*), cooled in a freezing mixture, was added dropwise with occasional shaking cold bromine (20.69g., 0.1297*M*). The brominated mixture was refluxed with a solution of NaOH (20g.) in ethanol for 15 hours. The oily portion was separated in the usual manner and agitated with cold 80% $H_2SO_4$. Saturates obtained amounted to *ca.* 2.2g. and this, when oxidised with potassium permanganate (Wallach, *loc. cit.*), afforded *p*- (α -hydroxypropyl[i])-benzoic acid, m.p. 156°, undepressed when admixed with an authentic sample of the acid. Further, potassium dichromate - sulphuric acid oxidation of 400mg. of the saturates furnished *ca.* 200mg. of terephthalic acid (dimethyl ester, m.p. 141°).

## DISCUSSION

Aromatisation of 3-carene (I) with bromine gave rise to *p*- and *m*- cymenes (VI & VII). Presence of these benzenoids was proved by their oxidation to terephthalic and isophthalic acids in amounts theoretically equivalent to 44.41% *p*-cymene and 13.47% *m*-cymene respectively. Thus it is evident that the terpene decyclises by fission of $C_1$-$C_7$ and $C_6$-$C_7$ linkages, and preferentially the former. The transformation clearly reveals the carbon framework in 3-carene, hitherto adduced from the results of its oxidative degradation (Simonsen, *loc. cit.*; Semmler and Schiller, *Ber.*, 1927, **60,** 1591) and hydrochlorination (Robinson, *Proc. Chem. Soc.*, 1911, **27,** 247). Up to the present, no terpenoid has simultaneously furnished these cymenes with bromine ; the

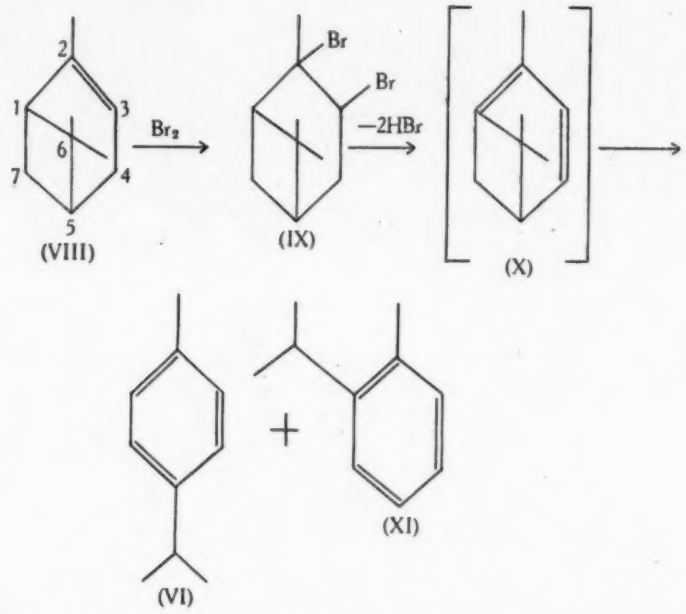
only terpenoid that afforded *m*-cymene, and that by the Baeyer-Villiger method (*Ber.*, 1898, **31,** 2067) is sylvestrene. Hence, the two-way aromatisation described herein constitutes a new reaction in terpene chemistry.

It has been reported earlier (Simonsen, *loc. cit.*) that with bromine in chloroform, 3-carene reacts readily, one mole of bromine being absorbed, but the dibromide is unstable and evolves hydrogen bromide. Now the addition of bromine to 3-carene, as described in the Experimental part, is also a smooth process, with very little evolution of hydrogen bromide. Fixation of bromine to the terpene can take place in two ways : (1) bromine saturates the double bond to yield the dibromide (II), assuming that the *cyclo*propane ring remains intact, and (2) bromine causes the cleavage of the *cyclo*propane ring two directionally at the $C_1$-$C_7$ and $C_6$-$C_7$ linkages to yield respectively the dibromides (III) and (IV). While the first possibility is in conformity with the normal addition of bromine to ethenoid linkage, the second possibility is justified because it is known that bromine can rupture *cyclo*propanes, as for instance in the conversion of *cyclo*propane into 1 : 3-dibromopropane (Gustavson, *J. prakt. Chem.*, 1900, *ii*, **62,** 290). On refluxing, the dibromide (II) gives off hydrogen bromide, as has been indicated in the experimental section, and is known from the observation made by Simonsen (*loc. cit.*) to afford, probably, 3 : 7 : 7-trimethyl-2 : 4-*nor*caradiene (V), which suffers two-directional cleavage of the *cyclo*propane ring to provide *p*- and *m*-cymenes. The dibromides (III) and (IV) can yield *p*- and *m*-cymene respectively by expelling two moles of hydrogen bromide and subsequent rearrangement.



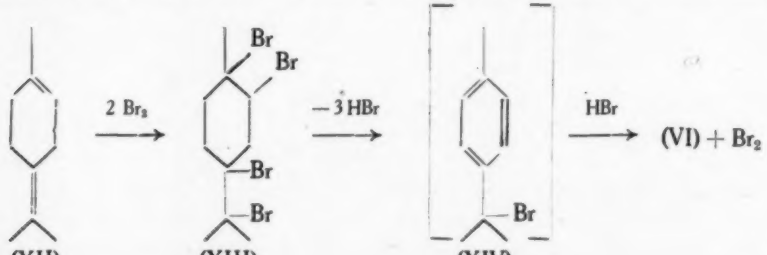

Coming to α-pinene (VIII), bromine is known to yield only *p*-cymene. This necessitates the unilateral fission of the $C_1$-$C_6$ bond of the terpene. Evidence is now presented to show that the $C_5$-$C_6$ bond can also break, leading to *o*-cymene (XI). Comparison of the yields of *tere*- and *ortho*-phthalic acids suggests that the favoured path of ring scission is at the $C_1$-$C_6$ bond. In the pinane series, reactions involving the formation of *o*-menthane derivatives are very rare (Perkin and Kay, *J. Chem. Soc.*, 1905, **87,** 1066 ; Simonsen, "The Terpenes", Vol. II, Cambridge University Press, 2nd ed., 1949, pp. 168, 170 ; cf. Verghese and Yeddanapalli, *J. Sci. Ind. Res.*, 1957, **16B,** 224 ; Verghese, *ibid.*, 1959, **18B,** 270 ; this *Journal*, 1959, **36,** 155 ; cf. Klein, Hunt and Booth, U.S.P., 2,818,435/1957), and so the two-way aromatisation is of considerable theoretical importance.

Moreover, this conversion reveals the mode of incorporation of the *cyclo*butane ring system in the methyl*cyclo*hexane nucleus in α-pinene.




The mechanism to account for this transformation of α-pinene can be formulated in a manner similar to that of 3-carene, and involves the addition of bromine across the double bond to yield the dibromide (IX), which then loses two moles of hydrogen bromide to furnish the transient compound (X). Formation of the multiple linkage at the bridgehead position is contrary to the Bredt rule (*Ber.*, 1902, **35,** 1286 ; *Annalen*, 1924, **437,** 1). Of the two modes of stabilisation of (X) by decyclisation, theoretically the fission of the linkage $C_1$-$C_6$ should take precedence over that of $C_5$-$C_6$. Actually this is the case. More *p*- than *o*-cymene is obtained in the reaction.

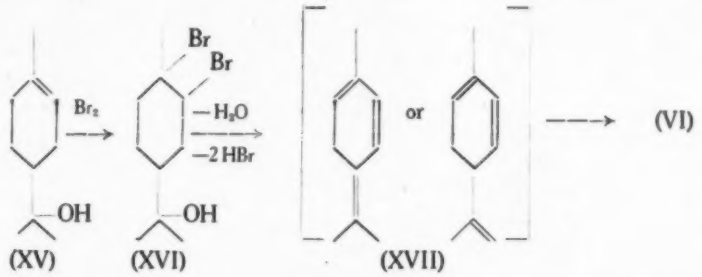
Attention may now be directed to the aromatisation of terpinolene (XII). Already Wallach (*Annalen*, 1893, **275,** 103) has indicated that the bromine atoms of terpinolene tetrabromide (XIII)




can be more easily cleaved than those of dipentene tetrabromide ; the hydrocarbon from terpinolene tetrabromide has not been studied though it seems to be *p*-cymene. Conclusive evidence is now presented to confirm this by preparation of the derivative, *p*- (α-hydroxypropyl[i])-benzoic

acid. Steps leading to *p*-cymene are shown in the above scheme. The decomposition consists of the expulsion of three moles of hydrogen bromide, and in the reductive elimination of the remaining bromine atom with the liberated hydrogen bromide ; the 8-bromo-*p*-cymene is only a hypothetical reaction intermediate.

Lastly, the aromatisation of terpineol (XV) may be considered. Saturation of the double bond in terpineol gives the dibromide (XVI), and this with alkali suffers dehydrobromination, dehydration, and then rearrangement to furnish *p*-cymene :




It may not be out of place to point out that Simonsen ("The Terpenes", Vol. I, Cambridge University Press, 2nd. ed., 1947, p. 262) has wrongly included this conversion among the examples of the Baeyer-Villiger method for dehydrogenation of cyclic bodies.

A common feature of these dehydrogenations is that excess of bromine has been strictly avoided. Thus, for 3-carene, α-pinene and terpineol, only molar proportion of bromine, which is half the quantity required for terpinolene, was used. Thus in agreement with Olsen (*loc. cit.*), the results of this investigation support the conclusion that the Baeyer-Villiger method is based on false premises and that there is no need to subject terpenoids to exhaustive bromination and later reduction for obtaining benzenoid counterparts.

The author acknowledges his indebtedness to Mr. T. S. Santhana Krishnan for collaboration in the early stages of this investigation. His thanks are also due to Prof. Rev. Fr. Lourdu M. Yeddanapalli, S. J., Head of the Dept. of Chemistry, Loyola College, Madras, and to Prof. S. C. Devadatta, Head of the Dept. of Chemistry, Christian Medical College, Vellore, for encouragement during the course of this work.

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# DETERMINATION OF IODOFORM BY PHOTO-OXIDATION IN ARTIFICIAL LIGHT

By R. M. Verma and Sameer Bose

A procedure for the determination of iodoform is described. It is based on the rapid decomposition of iodoform into free iodine when exposed to artificial light of mercury vapour lamp. All the three atoms of iodine are quantitatively oxidised and the free iodine has been evaluated by thiosulphate. The maximum amount of iodoform estimated by this method is 0.1g. The analytical precision is 1% or better.

Iodoform absorbs light in the visible region (Ellis, Wells and Heyroth, "Chemical Action of Ultraviolet Light", 1941, p. 395). Emschwiller (*Bull. Soc. Chim.*, 1939, **6,** 551) observed the formation of iodine pentoxide on photo-oxidation. He subsequently attributed the formation of iodine pentoxide to the secondary reaction, the primary product of photo-oxidation being free iodine (*Compt. rend.*, 1938, **207,** 1201). Bose developed a procedure (*Anal. Chem.*, 1958, **30,** 1137) for the evaluation of iodoform involving its quantitative decomposition into free iodine, when a solution in ether-benzene mixture was exposed to bright sunlight. As sunlight is not always available in the laboratory the present work, using artificial light from a 80 watts mercury vapour lamp, has been undertaken.

## Experimental

Sodium thiosulphate, iodine, and starch used were of A.R. quality. Potassium iodide and iodoform were of Merck's chemically pure variety. The following solutions were prepared: 0.02 *N*-$I_2$, 0.1*N* and 0.02*N* thiosulphate, and 1% aqueous starch.

### *Effect of Solvent on Photo-oxidation of Iodoform by Mercury Vapour Lamp*

To find a suitable solvent for iodoform, the effect of various solvents on the process of photo-oxidation in artificial light was investigated. 0.05% Iodoform solutions were prepared in ether, benzene, chloroform, and $CCl_4$ and 100 c.c. of each was exposed to light from a mercury vapour lamp in a 250 c.c. conical flask, which was corked and swirled from time to time. The flask was kept as close to the lamp as possible (the distance between centres of the flask and the lamp was about 5″). Time of exposure was one hour after which 1 g. of solid potassium iodide and the starch solution were added, and the liberated iodine was titrated with 0.02*N* thiosulphate solution.

TABLE I

| Solvent. | Initial rate of decomposition. | Iodoform. Present. | Found. |
|---|---|---|---|
| Ether | Very rapid | 50.0 mg. | 40.50 mg. |
| Benzene | Rapid | 50.0 | 49.80 |
| Chloroform | Slow | 50.0 | 49.21 |
| Carbon tetrachloride | Do | 50.0 | 49.28 |

(1 c.c. of 0.02*N* thiosulphate soln. ≡ 2.626 mg. of iodoform)

In ether solution the decomposition was initially very rapid, but the solution soon developed a brownish red colour, and the decomposition of iodoform was not carried to completion as the red colour of the solution acted as an autofilter preventing further action (red light was found experimentally to inh.bit the photochemical oxidation of iodoform). In $CHCl_3$ and $CCl_4$ solutions the rate of decomposition was slow and solutions developed a colour with a purple tinge, but the

oxidation was complete in one hour. As ether is very volatile, a mixture of ether and benzene has been found to be the most suitable. Moreover, $CCl_4$ and $CHCl_3$ being heavier than water settle down preventing the access of oxygen.

*Effect of Light of Different Wave Lengths*

The effect of light filters on the rate of decomposition of iodoform was also studied using glass filters in presence of various solvents, as shown in Table II. Red filter slowed down the photo-oxidation considerably. This bears the contention of autofilter in the case of ether solution.

A 0.2% solution of iodoform (50 c.c.) in different solvents was exposed to light of different wave lengths under identical conditions, keeping the time of exposure and distance between the lamp and the flask the same.

TABLE II

Exposure = 30 mins. $CHI_3$ taken=100 mg.

| No. | Wave length of filters. | Iodoform found (mg.) in | | | |
|---|---|---|---|---|---|
| | | Ether. | Benzene. | $CCl_4$. | $CHCl_3$. |
| 1. | No filter | 39.4 | 84.0 | 78.1 | 75.5 |
| 2. | 640 to 700 mμ (red) | 17.0 | 32.8 | 20.3 | 38.1 |
| 3. | 580 to 600 (yellow) | 28.9 | 74.1 | 63.6 | 63.0 |
| 4. | 520 to 580 (green) | 28.6 | 70.8 | 52.5 | 59.1 |
| 5. | 400 to 450 (blue) | 35.1 | 76.8 | 64.8 | 65.0 |

*Determination of Ethanol Solution of Iodoform*

A solution of iodoform (5-10 c.c.) in ethanol containing not more than 0.1 g. of the substance was pipetted into a 250 c.c. conical flask, and 15 c.c. each of benzene and ether were added. 0.1 *N* Sodium thiosulphate (10 c.c.) and water (100 c.c.) were also introduced into the flask, which was kept close to the mercury lamp (the distance between the centres of the flask and the lamp was about 5" to 6") . A brownish red colour was observed in the non-aqueous layer due to decomposition of iodoform into free iodine. The flask was shaken from time to time so that the liberated iodine was reduced by sodium thiosulphate solution. This prevented the ether-benzene layer from acquiring a red colour and acting as an autofilter. The flask was shaken once every minute for first 10 minutes, then once every two minutes for next 10 minutes, and later once every five minutes till the non-aqueous layer became colorless. It was then kept under observation for 2 minutes without shaking. The ether-benzene layer during this period developed no colour, indicating complete oxidation. The total time of exposure required for complete photo-oxidation depends upon the following conditions :

1. The amount of iodoform present.
2. The distance of the flask from the mercury vapour lamp.
3. Temperature of the water added.
4. The amount of water added.

Undue long exposures were found to afford higher values for iodoform. Accurate results may be obtained by carrying out experiments with known amounts of iodoform, weights of which are comparable.

After the photo-oxidation was over, the flask was removed from the lamp, and the excess of sodium thiosulphate was titrated with 0.02*N* iodine solution after adding 1 g. of solid potassium iodide and 1 c.c. of starch solution. A blank was also carried out in a similar manner except for the addition of iodoform solution. The difference in the two readings gave the amount of iodine liberated from iodoform.

To avoid any reaction between ether and sodium thiosulphate in light, a dilute solution of sodium thiosulphate was used (reaction is negligible with 0.01*N* thiosulphate). The oxygen present in about 120 c.c. of air enclosed in the flask was found to be enough for the photo-oxidation of 0.1g. of iodoform. (1 c.c. of 0.1 *N* iodine solution ≡ 13.133 mg. of iodoform).

TABLE III

*Estimation of iodoform dissolved in ethanol.*

| Expt. No. | Exposure. | Iodoform. | | % Error. |
|---|---|---|---|---|
| | | Present. | Found. | |
| 1. | 30 mins. | 100.0 mg. | 99.88 mg. | −0.12 |
| 2. | 30 | 90.0 | 89.77 | −0.30 |
| 3. | 25 | 80.0 | 79.73 | −0.30 |
| 4. | 25 | 70.0 | 70.48 | +0.60 |
| 5. | 20 | 60.0 | 60.50 | +0.80 |
| 6. | 15 | 50.0 | 50.40 | +0.80 |

*Estimation of Iodoform suspended in Water.*—Suspensions were prepared by weighing iodoform into a 250 c.c. conical flask containing about 100 c.c. of water to which 20 c.c. ether was added. The flask was corked and vigorously shaken till iodoform dissolved completely. About 10 c.c. of benzene and 10 c.c. of 0.1 *N* sodium thiosulphate (by pipette) were added. The flask was exposed to light from the mercury vapour lamp and the amount of iodoform was determined in a manner similar to that already described. A blank was carried out using 100 c.c. of water instead of the suspension.

TABLE IV

| Expt. No. | Water. | Exposure. | Iodoform. | | % Error. |
|---|---|---|---|---|---|
| | | | Present. | Found. | |
| 1. | 50 c.c. | 25 mins. | 100.0 mg. | 100.14 mg. | +0.14 |
| 2. | 100 | 30 | 100.0 | 99.48 | −0.50 |
| 3. | 100 | 30 | 80.0 | 80.45 | +0.60 |
| 4. | 100 | 25 | 70.0 | 70.48 | +0.60 |

The determination of iodoform by the method described is rapid and simple. It can be used for estimating solutions of organic compounds (such as acetone) which undergo quantitative iodoform reaction. The method is independent of sunlight as mercury vapour lamp has been used as a substitute. The disadvantage is the expected interference by other iodine-substituted organic compounds as most of them are affected by light.

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# CHEMISTRY OF VANADIUM. PART V. FORMATION OF COMPOUNDS OF VANADIUM OXYTRICHLORIDE WITH PHENOLS

By Sarju Prasad and Kailash Nath Upadhyaya

Two series of compounds have been prepared by the action of vanadium oxytrichloride on phenols in $CCl_4$, one at the room temperature and the other by refluxing at higher temperatures. The properties of the compounds have been studied and their structures discussed.

No systematic work appears to have been done on the formation of compounds of vanadium oxytrichloride with phenols, substituted or otherwise, excepting that by Funk *et al.* (*Z. anorg. Chem.*, 1958, **296**, 36). They studied the formation of compounds of $VOCl_3$ with organic substances including a few phenols, and obtained the compounds, $VOCl(OPh)_2.VO(OPh)_3$, $VO(p\text{-}ClC_6H_4O)_3$, and $VO(o\text{-}ClC_6H_4O)_3$.

The present investigation was therefore undertaken with a view to studying the formation of compounds of $VOCl_3$ with phenols under different conditions.

## Experimental

Vanadium oxytrichloride was prepared by the method of Roscoe (*J. Chem. Soc.*, 1868, **21**, 342) and purified by distillation. It was redistilled over metallic sodium and extracted with $CCl_4$. The chemicals used were of B.D.H. or E. Merck's 'extra pure' quality. Phenols and nitrophenols were recrystallised before use.

*Procedure.*—Two series of experiments were carried out. In one an excess of phenol solution in $CCl_4$ was added to $VOCl_3$ solution in $CCl_4$ and the mixture kept at the room temperature for 8 to 10 hours with frequent shaking till the evolution of HCl had ceased with the separation of a precipitate. In the other, a mixture of $VOCl_3$ and an excess of phenol in $CCl_4$ was warmed at 50-60° in an oil bath for about an hour and then refluxed at a temperature slightly higher than the melting point of the corresponding phenol till the evolution of HCl had ceased. The products obtained in both the cases were washed free of phenol with $CCl_4$, dried at about 45-50°, analysed, and their properties studied.

Vanadium was estimated in dilute $H_2SO_4$ by reduction with $SO_2$, removal of $SO_2$ by $CO_2$ and titration with $KMnO_4$ solution at 70°. Chlorine was estimated as AgCl and nitrogen by Duma's method in Gallenkamp's electric furnace. Carbon and hydrogen were estimated by the combustion method in a few cases. Colour and analytical data of the compounds in the various phenols are recorded in Tables I and II.

*General Properties.*—All the compounds are dark in colour, crystalline, insoluble in common organic solvents except ethanol and acetone in which these are sparingly soluble. These are also soluble in strong alkali solutions. The compounds obtained at the room temperature hydrolyse slowly when treated with dilute alkali solutions or water, and the water extract responds to the test of $Cl^-$; but those obtained by refluxing are not affected. These do not give sharp melting points but decompose when heated.

## TABLE I

*Compounds of* $VOCl_3$ *with phenols.*
(At room temperature).

| Phenols. | Colour. | %Vanadium. Found. | %Vanadium. Calc. | %Chlorine. Found. | %Chlorine. Calc. | %Carbon & hydrogen. Found. | %Carbon & hydrogen. Calc. | %Nitrogen. Found. | %Nitrogen. Calc. | Probable formulas. |
|---|---|---|---|---|---|---|---|---|---|---|
| α-Naphthol | Greenish black | 13.01 | 13.13 | 9.16 | 9.14 | C: 61.42 H: 3.57 | 61.80 3.60 | .. | .. | $VOCl(C_{10}H_7O)_2$ |
| β-Naphthol | Greyish black | 13.07 | 13.13 | 9.17 | 9.14 | .. | .. | .. | .. | ,, |
| o-Cresol | Greyish brown | 16.26 | 16.12 | 11.19 | 11.22 | C: 45.90 H: 4.46 | 45.50 4.42 | .. | .. | $VOCl(CH_3C_6H_4O)_2$ |
| o-Nitrophenol | Dark brown | 13.53 | 13.48 | 9.35 | 9.38 | .. | .. | 7.33 | 7.39 | $VOCl[C_6H_4(NO_2)O]_2$ |
| m- ,, | Brownish black | 13.51 | 13.48 | 9.34 | 9.38 | C: 37.77 H: 3.66 | 38.04 3.70 | 7.35 | 7.39 | ,, |
| p- ,, | Light black | 13.43 | 13.48 | 9.42 | 9.38 | .. | .. | 7.33 | 7.39 | ,, |
| 2:4-Dinitrophenol | Greyish brown | 10.92 | 10.88 | 7.61 | 7.57 | .. | .. | 11.46 | 11.95 | $VOCl[C_6H_3(NO_2)_2O]_2$ |
| 2:4-Dinitronaphthol | Reddish brown | 8.91 | 8.85 | 6.12 | 6.16 | C: 41.88 H: 1.71 | 41.63 1.73 | 9.75 | 9.71 | $VOCl[C_{10}H_5(NO_2)_2O]_2$ |
| Catechol | Brownish black | 24.01 | 24.23 | 16.94 | 16.87 | C: 34.46 H: 1.88 | 34.21 1.90 | .. | .. | $VOCl.C_6H_4O_2$ |
| Resorcinol | Light black | 24.04 | 24.23 | 16.93 | 16.87 | .. | .. | .. | .. | ,, |
| Hydroquinone | Dark grey | 24.28 | 24.23 | 16.84 | 16.87 | .. | .. | .. | .. | ,, |
| Pyrogallol | Greyish black | 22.46 | 22.51 | 15.72 | 15.67 | C: 31.49 H: 1.81 | 31.78 1.77 | .. | .. | $VOCl.C_6H_3O_2(OH)$ |
| Phloroglucinol | Chocolate brown | 22.57 | 22.51 | 15.70 | 15.67 | .. | .. | .. | .. | ,, |

## TABLE II

*Compounds of* $VOCl_3$ *with phenols.*
(After refluxing).

| Phenols. | Colour. | %Vanadium. Found. | %Vanadium. Calc. | %Carbon. Found. | %Carbon. Calc. | %Hydrogen. Found. | %Hydrogen. Calc. | %Nitrogen. Found. | %Nitrogen. Calc. | Probable formulas. |
|---|---|---|---|---|---|---|---|---|---|---|
| α-Naphthol | Brownish black | 10.25 | 10.28 | 72.38 | 72.58 | 4.16 | 4.23 | .. | .. | $VO(C_{10}H_7O)_3$ |
| β-Naphthol | Dark brown | 10.31 | 10.28 | .. | .. | .. | .. | .. | .. | ,, |
| o-Cresol | Chocolate brown | 13.26 | 13.15 | 64.62 | 64.96 | 5.35 | 5.41 | .. | .. | $VO(C_6H_4.CH_3O)_3$ |
| o-Nitrophenol | Pitch black | 10.57 | 10.60 | .. | .. | .. | .. | 8.67 | 8.73 | $VO(C_6H_4.NO_2.O)_3$ |
| m- ,, | Brownish black | 10.58 | 10.60 | .. | .. | .. | .. | 8.66 | 8.73 | ,, |
| p- ,, | Deep brown | 10.63 | 10.60 | 45.00 | 44.92 | 2.51 | 2.49 | 8.69 | 8.73 | ,, |
| 2:4-Dinitrophenol | Brownish black | 8.21 | 8.24 | 34.43 | 34.90 | 2.01 | 1.99 | 13.61 | 13.57 | $VO[C_6H_3(NO_2)_2O]_3$ |
| 2:4-Dinitronaphthol | Reddish brown | 6.59 | 6.56 | .. | .. | .. | .. | 13.75 | 10.80 | $VO[C_{10}H_5(NO_2)_2O]_3$ |
| Resorcinol | Dark brown | 22.14 | 22.26 | 46.92 | 47.17 | 2.58 | 2.62 | .. | .. | $(VO)_2(C_6H_4O_2)_3$ |
| Hydroquinone | Shining black | 22.08 | 22.26 | .. | .. | .. | .. | .. | .. | ,, |
| Pyrogallol | Dark grey | 22.21 | 20.15 | 42.35 | 42.69 | 2.41 | 2.37 | .. | .. | $(VO)_2(C_6H_3O_2OH)_3$ |
| Phloroglucinol | Deep brown | 20.02 | 20.15 | .. | .. | .. | .. | .. | .. | ,, |

## DISCUSSION

An examination of the results shows that two series of compounds of substitution type are formed when $VOCl_3$ is allowed to react with phenols. The replacement of chlorine atoms takes place in two stages. At the room temperature two chlorine atoms are replaced by one molecule of a dihydroxyphenol or two molecules of a monohydroxyphenol, the reaction being completed more quickly with the former. These compounds may be represented as $VOCl(PhO)_2$ with monohydroxy- and $VOCl(PhO_2)$ with dihydroxy-phenols.

On refluxing three molecules of a monohydroxyphenol react with one molecule of $VOCl_3$, and three molecules of a dihydroxyphenol (except catechol) with two molecules of $VOCl_3$, and chlorine is replaced completely. These compounds may be represented as $VO(PhO)_3$, and $(VO)_2(PhO)_3$ with mono- and dihydroxyphenols respectively. The anomalous behaviour of catechol, with which no pure compound was obtained, may be due to steric hindrance, which is in accordance with the observations of Funk *et al.* (*loc. cit.*).

The analysis of both the types of compounds obtained with trihydroxyphenol shows that only two hydroxyl groups take part in these reactions. From the experiments carried out it is not possible to find the position of free OH group, and therefore no definite formula can be assigned to them.

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# BERYLLIUM FLUORIDES. PART IV. FLUOBERYLLATO-OXALATES

By Apurba Kumar Sengupta*

Fluoberyllato-oxalates of sodium, potassium, and ammonium have been described. The salts can be prepared starting either from beryllium fluoride, or from beryllium oxalate. The formation and stability of fluoberyllato-oxalate ion have been studied by thermometry, conductometry and cryoscopically.

Beryllium fluoride in the solid state has been shown to be polymorphic and polymeric in nature having modifications isomorphous with silica in quartz and β-crystobalite forms (Warren and Hill, *Z. Krist.*, 1934, **89**, 481; Novoselova and Zimanov, "Uchenye Zapiski Moskov. Gosudarst. Univ. im M.V. Lomonosova", 1955, No. 174, p 7). But in aqueous solution, which reacts faintly acidic due to hydrolysis, it exists mainly as a non-electrolyte, $[BeF_2, 2H_2O]^\circ$ (Linnell and Haendler, *J. Phys. Coll. Chem.*, 1948, **52**, 819). Behaving as a Lewis acid it is known to co-ordinate with more fluoride ions, which act as a Lewis base, to yield the well-known tetrafluoberyllates. Beryllium fluoride has also been reported to co-ordinate with ammonia at a low temperature to yield $BeF_2.NH_3$ (Biltz and Rahlfs, *Z. anorg. Chem.*, 1927, **166**, 355). The present author therefore in exploring this electron-acceptor property of beryllium fluoride has been able to isolate the fluoberyllato-oxalates only.

In a similar way, weakly conducting beryllium oxalate, $BeC_2O_4.3H_2O$, can also be presumed as the monomolecular non-electrolyte, $[(C_2O_4)Be(H_2O)_2]$, the third water molecule being connected with oxalate group. Therefore the preparation of fluoberyllato-oxalates, starting from beryllium oxalate, has also been examined.

## Experimental

Beryllium fluoride was prepared from $(NH_4)_2BeF_4$ according to Lebeau (*Compt. rend.*, 1898, **126**, 1418). In preparing beryllium oxalate, $BeC_2O_4.3H_2O$, Parson's method (*J. Amer. Chem. Soc.*, 1906, **28**, 555) was followed.

The conductances were measured in a plastic vessel with a Kohlrausch Universal Bridge, Cat. No. 7401, W. G. Pye and Co. Ltd., Cambridge, England. The glass stems of the two platinised electrodes were carefully covered with wax prior to platinising the electrodes. The thermometric titration and the determination of freezing point were done as usual.

*Potassium Fluoberyllato-oxalate*, $K_2BeF_2(C_2O_4).H_2O$.—On titrating thermometrically (Table I) a beryllium fluoride solution by potassium oxalate solution, temperature was found first to decrease slowly, and then increase sharply from $BeF_2 : K_2C_2O_4 = 1 : 1$. These results show that the initial fall of temperature during the titration is caused by the reaction leading to compound formation, which is endothermic, and the subsequent rise by the crystallisation of the compound from the solution, which is exothermic. After the titration was over, crystals were found in the Dewar flask. The crystals were filtered by suction, washed, dried in air, and analysed. (Found : K, 33.97 ; Be, 4.11 ; F, 16.31 ; $C_2O_4$, 38.11. $K_2BeF_2(C_2O_4).H_2O$ requires K, 33.82 ; Be, 3.90 ; F, 16.44 ; $C_2O_4$ 38.06%).

TABLE I

0.4404*M*-$BeF_2$ taken = 500 c.c. $K_2C_2O_4$ soln. added = 2*M*.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pot. oxalate (c.c.) | .. | 0 | 1 | 2 | 4 | 6 | 8 | 10 | 12 |
| Beckman reading | .. | 3.61 | 3.628 | 3.66 | 3.765 | 3.87 | 3.906 | 3.955 | 1.48 |
| Change in temp. | .. | .. | −0.018 | −0.05 | −0.155 | −0.26 | −0.296 | −0.345 | +2.475 |

The above compound can suitably be prepared as follows. To a continuously stirred beryllium fluoride solution (18 c.c.), containing 3.5 g. $BeF_2$, potassium oxalate solution (50 c.c., containing

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14.5 g. $K_2C_2O_4.H_2O$) was added, when immediately crystals appeared. The solution was then cooled with ice to *ca.* 10°, and filtered by suction. The rhombic crystals were washed successively with ice-cold water and ethanol, and dried in air; yield 15.3 g. The substance was recrystallised from water. [Found (recrystallised sample): Be, 3.98%; $C_2O_4$, 38.03%]. The solubility of the compound, $K_2BeF_2(C_2O_4).H_2O$, at 29.5° was found to be 3.33 g./100 c.c.

The above compound was also prepared from beryllium oxalate in the above manner by adding a potassium fluoride solution (10 c.c., containing 1.4 g. KF) to beryllium oxalate solution (10 c.c., containing 1.8 g. of $BeC_2O_4,3H_2O$). As before, immediately crystals separated, and the solution became hot. After cooling the solution to room temperature, the crystals were filtered by suction, washed with ice-cold water, then with ethanol, and dried in air; yield 1.94 g. (Found: Be, 4.06; F, 16.28; $C_2O_4$, 38.05%).

*Ammonium Fluoberyllato-oxalate*, $(NH_4)_2BeF_2(C_2O_4).H_2O$.—A beryllium fluoride solution (7.5 c.c., containing 1.5 g. $BeF_2$) was added to an ammonium oxalate solution (70 c.c.), containing 5 g. $(NH_4)_2\ C_2O_4.H_2O$, with stirring, when a faint turbidity appeared. The solution was filtered, and the filtrate was allowed to crystallise in a desiccator over $H_2SO_4$. After several days crystals of ammonium oxalate that appeared were filtered off, and the filtrate was allowed to crystallise again. After rejecting the second crop, the third crop of crystals (rhombic), which were different from the previous ones, were filtered, washed successively with ice-cold water and ethanol, and dried in air; yield 1.7 g. [Found: N, 14.73; Be, 4.66; F, 19.63; $C_2O_4$, 46.43. $(NH_4)_2BeF_2$-$(C_2O_4).H_2O$ requires N, 14.81; Be, 4.77; F, 20.1; $C_2O_4$, 46.56%]. Solubility of the ammonium compound was determined to be 16.42 g. of $(NH_4)_2\ BeF_2(C_2O_4).H_2O$ per 100 c.c. water at 23.5°.

*Sodium Fluoberyllato-oxalate*, $Na_2BeF_2(C_2O_4)$, $1.8H_2O$.—The sodium salt was prepared in the same way as the ammonium salt. [Found: Na, 21.81; Be, 4.23; $C_2O_4$, 41.23. $Na_2BeF_2$-$(C_2O_4)$, 1.8 $H_2O$ requires Na, 21.56; Be, 4.22; $C_2O_4$, 41.24%]. The compound was found to lose water at the room temperature.

Lead, calcium, silver, nickel, copper, and cobalt (II) salts of the present series could not be isolated by metathetical reactions with the potassium fluoberyllato-oxalate since the corresponding metallic oxalates or fluorides precipitated out.

Besides the thermometric titration (*vide supra*), the formation of the complex fluoberyllato-oxalate ion has also been indicated by the increase in solubility of ammonium and sodium oxalates in beryllium fluoride solution (vide the preparation of the $NH_4$ and Na fluoberyllato-oxalates). The complex ion has been studied by measurement of the conductance of fluoberyllato-oxalate solutions at different dilutions, and of freezing point depression of water.

For the conductometric measurements (Table II) solutions of potassium fluoberyllato-oxalate (recrystallised) at different dilutions were prepared in wax-coated tubes. The conductances were measured immediately after preparation of the solutions, and after twelve days; but no difference was found.

TABLE II

*Conductance of potassium fluoberyllato-oxalate solns. at diff. dilutions.*

| $v$ (dilution) | 16 | 32 | 64 | 128 | 256 | 512 | 1024 | 2048 |
|---|---|---|---|---|---|---|---|---|
| $\mu_v$ (at 31°) (immediate) | .. | 228.2 | 250 | 265.6 | 280 | 291.4 | 311 | 335.8 |
| $\lambda_v$ | 114.1 | 124.9 | 132.8 | 139.9 | 145.7 | 155.5 | 167.9 | .. |
| $\lambda_\infty$ | 153.6 | 155.5 | 155.8 | 157.0 | 158.3 | 165.0 | 175.1 | .. |

The $\lambda_\infty$ values have been calculated from Walden's formula $\lambda_\infty = \lambda_v\ (1 + n_1n_2 \times 0.692 \times v^{-\frac{1}{2}})$, where $v$ = dilution, $n_1$ and $n_2$ are the valencies of the ions.

A comparison of the above molecular conductances with those of potassium sulphate solutions indicates that the fluoberyllato-oxalate dissociates into a monovalent cation and a divalent anion. The $\lambda_\infty$ values suggest a further dissociation of the complex anion, of which the valency has been calculated to be 2.079 (*i.e. ca.*2) applying Walden's formula (*vide supra*) and utilising $\lambda_v$ values at 32 and 64 dilutions, *i.e.* where $\lambda_\infty$ values have been found to be almost the same.

TABLE III

*Lowering of f. p. of water by* $K_2BeF_2(C_2O_4).H_2O$.

$K_2BeF_2(C_2O_4).H_2O$ taken in 50 c.c. of water $= x$ g.

| $x$. (g.) | F. P. (Beckmann reading) | Lowering of f.p. ($d$) | M.W. ($m$) | No. of ions. ($n$) |
|---|---|---|---|---|
| 0.0 | 2.155 | .. | .. | .. |
| 0.4838 | 2.423 | 0.268 | 67.07 | 3.446 |
| 0.8033 | 2.563 | 0.408 | 73.14 | 3.160 |

The measurement of lowering of f. p. of water by potassium fluoberyllato-oxalate (Table III) shows that the compound dissociates into three ions, probably in the following way:

$$K_2BeF_2(C_2O_4) = 2\,K^+ + [BeF_2(C_2O_4)]^{2-}$$

But there is also a secondary dissociation of the complex anion as evidenced by the value of $n$ slightly $> 3$, and this result is in accord with that found by conductometric studies (*vide supra*). As the chemical reactions of $Ni^{2+}$, $Cu^{2+}$ etc. (*vide supra*), and their pyridine complex cations yield precipitates of the corresponding oxalates from fluoberyllato-oxalates, the complex anion can be presumed to dissociate as follows:

$$[BeF_2(C_2O_4)]^{2-} \rightleftharpoons BeF_2 + C_2O_4^{2-}$$

These experiments therefore indicate that fluorine is more strongly bound to beryllium than oxalate.

Attempts have also been made by the present author to isolate analogous fluoberyllato anions containing salicylate, malonate, formate, acetate or chloroacetate groups by mixing beryllium fluoride and the corresponding sodium or potassium salts of the respective acids, but in no case the ions aimed at could be isolated. In the case of salicylate, it was found that on mixing beryllium fluoride and potassium salicylate, salicylic acid precipitated out.

It was found that on adding acetylacetone to beryllium fluoride solution no reaction took place as was evidenced by the existence of two immiscible layers of liquids. When ammonia was added to this mixture, beryllium acetylacetonate crystallised out.

Author's best thanks are due to Prof. P. B. Sarkar, Dr. es. Sc., Head of the Department of Pure Chemistry, for his kind suggestions, encouragement and providing all laboratory facilities. Author is also greatly indebted to Sri N. N. Ghosh for his kind suggestions.

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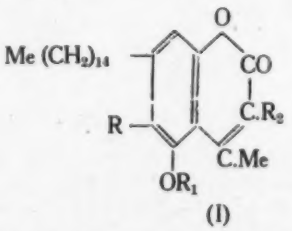
# COUMARINS FROM 5-*n*-PENTADECYLRESORCINOL AND THE FRIES REACTION OF THEIR ESTERS

By B. M. Desai and (Miss) Pushpa R. Desai

5-Hydroxycoumarin derivatives have been obtained by the interaction of 5-*n*-pentadecylresocinol with ethyl acetoacetate, ethyl methylacetoacetate and ethyl ethylacetoacetate. The Fries reaction of the acetoxycoumarins in presence of anhydrous aluminium chloride has been studied.

Rasinski (*J. prakt. Chem.*, 1882, *ii*, **26,** 59) obtained a ketone by condensing orcinol with glacial acetic acid in presence of phosphorus oxychloride. This ketone later was proved to be 2 : 6-dihydroxy-4-methylacetophenone by Ludwinowsky and Tambor (*Ber.*, 1906, **39,** 4047). Shah *et al.* (*J. Chem. Soc.*, 1938, 228, 1066 ; *Nature*, 1938, **142,** 163) have brought forward the evidence of γ-substitution in resorcinol derivatives. Baker (*J. Chem. Soc.*, 1934, 1684 ; 1935, 628 ; 1937, 479) observed that certain resacetophenone derivatives underwent γ-substitution. Desai *et al.* (*Proc. Ind. Acad. Sci.*, 1938, **8A,** 194 ; 1940, **12A,** 391) showed that resacetophenone and orcinol underwent γ-substitution side by side with β-substitution. Orcinol also furnished a case of γ-substitution when condensed with succinic anhydride in presence of anhydrous aluminium chloride (Desai and Shroff, *J. Univ. Bombay*, 1941, **10,** Part III, 97).

Orcinol undergoes the Pechmann reaction with open-chain as well as cyclic β-ketonic esters, yielding 5-hydroxycoumarins, as observed by Dey (*J. Chem. Soc.*, 1915, **99,** 1614), and Ahmed and Desai (*Proc. Ind. Acad. Sci.*, 1937, **5A,** 227). We thought it interesting to study the Pechmann reaction of 5-*n*-pentadecylresorcinol as it contains the higher alkyl group, which we hoped would favour γ-substitution. We condensed 5-*n*-pentadecylresorcinol with ethyl acetoacetate, ethyl methylacetoacetate and ethyl ethylacetoacetate to obtain 5-hydroxycoumarin derivatives as these dissolved in alkali with a yellow colour. These were characterised by their acetyl and methoxy derivatives. The same coumarins were obtained when polyphosphoric acid was used instead of concentrated sulphuric acid.




R = H, COMe.
R1 = H, COMe.
R2 = Me, Et.

(I)

The Fries reaction of the esters of hydroxycoumarins was carried out by various workers (Desai *et al.*, *Proc. Ind. Acad. Sci.*, 1937, **6A,** 185 ; 1938, **8A,** 571 ; 1941, **14A,** 99 ; 1942, **15A,** 11 ; Shah *et al.*, *J. Chem. Soc.*, 1938, 228, 1424 ; 1939, 1250 ; Limaye *et al.*, *Rasayanam*, 1936, 20 ; 1937, 93 ; 1938, 141 ; 1939, 187). Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1947, **25A,** 32) have studied the Fries reaction of esters of 7-hydroxy-, 6-hydroxy-, 7 : 8-dihydroxy- and 6 : 7-dihydroxy-coumarins. Desai and Bhavsar (this *Journal*, 1954, **31,** 167) have studied the rearrangement of *p*-toluenesulphonates of 7-hydroxy- and 5-hydroxycoumarin derivatives. We have studied the Fries reaction of the acetyl derivatives of the coumarins obtained from 5-*n*-pentadecylresorcinol. The Fries reaction of 4-methyl-7-pentadecyl-5-acetoxycoumarin (I : R=H ;

$R_1$=COMe ; $R_2$=H) in presence of three mols. of anhydrous aluminium chloride furnished 4-methyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin (I : R= — COMe ; $R_1$= $R_2$=H), the acetyl group migrating to position 6. Similarly 3 : 4-dimethyl-7-pentadecyl-5-acetoxycoumarin (I : R= H ; $R_1$= — COMe ; $R_2$=Me) and 3-ethyl-4-methyl-7-pentadecyl-5-acetoxycoumarin (I : R=H ; $R_1$= — COMe ; $R_2$=Et) afforded 3 : 4-dimethyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin (I : R= —COMe; $R_1$=H; $R_2$=Me), and 3-ethyl-4-methyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin (I : R= —COMe ; $R_1$=H ; $R_2$=Et) respectively. These products develop a reddish coloration with ferric chloride solution, indicating the *ortho* positions of -OH and COMe groups.

In view of the investigation by Parkhi and Sethna (this *Journal*, 1960, **37**, 159) we are submitting some of our relevant results. Further work on the reactions of 5-*n*-pentadecylresorcinol is in progress.

## EXPERIMENTAL

*4-Methyl-7-pentadecyl-5-hydroxycoumarin.*—To 5-*n*-pentadecylresorcinol (3 g.), dissolved in ethyl acetoacetate (2 c.c.), $H_2SO_4$ (conc., 4 c.c.) was gradually added and the mixture left overnight. The mixture was poured over crushed ice, when a solid separated. It was filtered, dried and crystallised from dilute ethanol in white shining needles, m.p. 148°, yield quantitative. It shows a greenish coloration with ferric chloride solution and dissolves in dilute alkali, developing a yellow colour. (Found : C, 78.2 ; H, 10.3. $C_{25}H_{28}O_3$ requires C, 77.7 ; H, 9.9%).

Polyphosphoric acid (orthophosphoric acid 12 c.c. + $P_2O_5$ 15 g.) was added slowly to 5-*n*-pentadecylresorcinol (3 g.), dissolved in ethyl acetoacetate (3 c.c.). The mixture was heated in an oil bath at 120-30° for 2 hours with stirring and then poured over crushed ice, when a solid separated. It was filtered, dried and crystallised from dilute ethanol in shining needles, m.p. 148°.

*4-Methyl-7-pentadecyl-5-acetoxycoumarin*, prepared in the usual manner, was crystallised from ethanol in glistening needles, m.p. 88°. It showed no coloration with ferric chloride solution. (Found : C, 76.4 ; H, 9.9. $C_{27}H_{40}O_4$ requires C, 75.7 ; H, 9.4%).

*4-Methyl-7-pentadecyl-5-methoxycoumarin*, prepared by treating the coumarin (0.5 g.) with dimethyl sulphate (5 c.c.) in presence of anhydrous potassium carbonate, was crystallised from ethanol in small colorless needles, m.p. 86°. (Found : C, 78.6 ; H, 10.6. $C_{26}H_{40}O_3$ requires C, 78.0 ; H, 10.1%).

*4-Methyl-7-pentadecyl-5-benzoyloxycoumarin* was prepared by treating the coumarin (0.5 g.) with benzoyl chloride (5 c.c.) in presence of pyridine. It was crystallised from ethanol in shining white needles, m.p. 95°. (Found : C, 78.48 ; H, 9.63. $C_{32}H_{42}O_4$ requires C, 78.40 ; H, 8.57%).

3 : 4-*Dimethyl-7-pentadecyl-5-hydroxycoumarin.*—A mixture of 5-*n*-pentadecylresorcinol (3 g.), ethyl α-methylacetoacetate (2 c.c.), and $H_2SO_4$ (conc., 4 c.c.) was kept overnight. It was poured on crushed ice and the product obtained was filtered, dried, and crystallised from dilute ethanol in thin yellowish needles, m.p. 125°. It dissolves in dilute alkali with a yellow colour. (Found ; C, 78.60 ; H, 10.55. $C_{26}H_{40}O_3$ requires C, 78.0 ; H, 10.0%).

3 : 4-*Dimethyl-7-pentadecyl-5-acetoxycoumarin*, prepared as usual, was crystallised from ethanol in white nedles, m.p. 85°. (Found : C, 76.5 ; H, 9.6. $C_{28}H_{42}O_4$ requires C, 76.0 ; H, 9.5%).

*3-Ethyl-4-methyl-7-pentadecyl-5-hydroxycoumarin.*—A mixture of 5-*n*-pentadecylresorcinol (3 g.), ethyl α-ethylacetoacetate (3 c.c.) and $H_2SO_4$ (conc.) was kept overnight. The product separating on decomposition was filtered off, dried, and crystallised from ethanol in yellowish white

needles, m.p. 135°. It dissolves in dilute alkali with a yellow colour. (Found : C, 78.51 ; H, 10.42. $C_{27}H_{42}O_3$ requires C, 78.25 ; H, 10.05%).

*3-Ethyl-4-methyl-7-pentadecyl-5-acetoxycoumarin*, prepared as usual, was crystallised from ethanol in colorless needles, m.p. 95°. (Found : C, 76.25 ; H, 9.39. $C_{29}H_{44}O_4$ requires C, 76.31 ; H, 9.65%).

*Fries Migration*

*4-Methyl-7-pentadecyl-5-acetoxycoumarin : Formation of 4-Methyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin.*—An intimate mixture of the acetoxycoumarin (2 g.) and $AlCl_3$ (anhyd., 4 g.) was heated in an oil bath at 140° for 3 hours. The residue, obtained after decomposing the excess of $AlCl_3$ with ice-cold HCl, was purified by alkali. The solid obtained on acidifying the alkaline solution was filtered, dried, and crystallised from dilute ethanol in small colorless needles, m.p. 138°. It develops a reddish colour with ferric chloride solution. (Found : C, 75.64 ; H, 9.64. $C_{27}H_{40}O_4$ requires C, 75.70 ; H, 9.41%).

*3 : 4-Dimethyl-7-pentadecyl-5-acetoxycoumarin : Formation of 3 : 4-Dimethyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin.*—The solid obtained on treatment of the relative acetoxycoumarin, as above and purified in the same way, furnished colorless needles from ethanol, m.p. 195°. It also gave a similar colour reaction with $FeCl_3$. (Found : C, 76.36 ; H, 9.24. $C_{28}H_{42}O_4$ requires C, 76.0 ; H, 9.50%).

*3-Ethyl-4-methyl-7-pentadecyl-5-acetoxycoumarin : Formation of 3-Ethyl-4-methyl-6-acetyl-7-pentadecyl-5-hydroxycoumarin.*—The relative acetoxycoumarin on Fries migration, as above, furnished colorless needles from ethanol, m.p. 198°. It develops a reddish colour with $FeCl_3$. (Found : C, 76.67 ; H, 9.72. $C_{29}H_{44}O_4$ requires C, 76.31 ; H, 9.65%).

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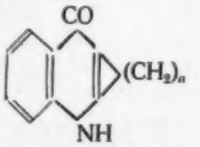
# HETEROCYCLIC COMPOUNDS. PART XXXIV. BROMINATION AND NITRATION OF 4-KETO-1:4-DIHYDRO-2:3-POLYMETHYLENEQUINOLINES

BY R. D. DESAI, B. M. DESAI AND (MISS) P. R. DESAI

Monobromination, dibromination, nitration and dinitration of 2-methyl-1:2:3:4-tetrahydroacridone (I), 4-keto-1:4-dihydro-2:3-pentamethylenequinoline (II) and 4-keto-1:4-dihydro-2:3-hexamethylenequinoline (III) have been studied. Compounds (II) and (III) have been synthesised by condensing anthranilic acid with *cyclo*heptanone and *cyclo*octanone respectively.

In continuation of our study on the bromination and nitration of 1-methyl- and 3-methyl-1:2:3:4-tetrahydroacridones (Desai *et al.*, this *Journal*, 1958, **35**, 88), we have extended this investigation to the case of 2-methyl-1:2:3:4-tetrahydroacridone, prepared from anthranilic acid and 3-methyl*cyclo*hexanone by Tiedke's method (*Ber.*, 1909, **42**, 621). As it was thought interesting to study the effect of a pentamethylene and a hexamethylene ring for comparison with that of the tetramethylene ring, which is present in the tetrahydroacridones, we have synthesised the requisite compounds by condensing anthranilic acid with *cyclo*heptanone and *cyclo*octanone respectively by the same method (*loc. cit.*). In each case the intermediate anils were isolated at low temperatures, and their cyclisation at high temperature afforded the desired products. These compounds have been named as the derivatives of dihydroquinoline. Thus, compound (II) is named as 4-keto-1:4-dihydro-2:3-pentamethylenequinoline, and compound (III) as 4-keto-1:4-dihydro-2:3-hexamethylenequinoline. Tetrahydroacridone itself can be named for comparison as 4-keto-1:4-dihydro-2:3-tetramethylenequinoline (I).




(I : $n$=4)
(II : $n$=5)
(III : $n$=6)

Bromination of 2-methyl-1:2:3:4-tetrahydroacridone afforded a mixture of 7-bromo and 9-bromo derivatives, and a 7:9-dibromo derivative on dibromination. Similarly bromination of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline furnished mainly the 8-bromo derivative accompanied by a small amount of 6-bromo isomer. 4-Keto-1:4-dihydro-2:3-hexamethylenequinoline on bromination gave also a mixture of equal amounts of 6-bromo and 8-bromo derivatives, while 6:8-dibromo derivatives were obtained in each case on dibromination.

2-Methyl-1:2:3:4-tetrahydroacridone on nitration afforded an equimolecular mixture of 7-nitro and 9-nitro derivatives, while 7:9-dinitro derivative was obtained on dinitration. Similarly 4-keto-1:4-dihydro-2:3-pentamethylenequinoline and 4-keto-1:4-dihydro-2:3-hexamethylenequinoline on nitration gave a mixture of 6-nitro and 8-nitro derivatives wherein the 8-nitro isomer predominated, while dinitration gave 6:8- dinitro derivative in each case. The authentic specimens for comparison were prepared by condensing appropriately substituted anthranilic acids with 3-methyl*cyclo*hexanone, *cyclo*heptanone, and *cyclo*octanone respectively.

## EXPERIMENTAL

1-o-*Carboxyanilino-5-methyl-* $\Delta^{1:2}$ *- cycloheptene.*— A mixture of anthranilic acid (5 g.) and *cyclo*heptanone ( 5 g. ) was heated in an oil bath at 120° for 3 hours. The product was washed with a little benzene to remove the impurities, and the residue was crystallised from benzene in colorless prisms, m.p. 140°, yield 6 g. (Found : C, 72.5 ; H, 7.1. $C_{14}O_{17}O_2N$ requires C, 72.7; H, 7.4%).

*4-Keto-1:4 dihydro-2:3-pentamethylenequinoline.*— The above anil was heated in an oil bath at 220° for 2 hours. The solid after treating with a dilute $NaHCO_3$ solution to remove the unchanged material was crystallised from benzene in small colorless plates, m.p. 335°. (Found: C, 78.0 ; H, 6.5 ; N, 6.32. $C_{14}H_{15}ON$ requires C, 78.9 ; H, 7.0 ; N, 6.57%).

*6 - & 8 - Bromo-4-keto-1:4-dihydro-2:3-pentamethylenequinolines.*—A solution of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline ( 4.26 g. ) in glacial acetic acid (20 c.c.) with a trace of iodine was cooled to 5°. A 20% solution of bromine in glacial acetic acid (8 c.c.) was next added gradually with stirring. After stirring the mixture for one hour at 10°, it was kept in an ice box for 24 hours and poured into water. The solid separating was filtered off, washed, dried, and finally crystallised from 90% ethanol in colorless needles, m.p. 329°, yield 2.56 g. This was proved to be the 8-bromo derivative by its mixed m.p. with the authentic specimen synthesised from 3-bromoanthranilic acid and *cyclo*heptanone. (Found : Br, 27.27. $C_{14}H_{14}ONBr$ requires Br, 27.49%).

The mother liquor on concentration gave a solid, which after several crystallisations from ethanol furnished brownish white needles, m.p. 340°, yield 0.12 g. This was shown to be 6-bromo derivative by its mixed m.p. with the authentic specimen obtained from 5-bromoanthranilic acid and *cyclo*heptanone. (Found: Br. 27.29. $C_{14}H_{14}ONBr$ requires Br, 27.49%).

*Synthesis of 6-Bromo-4-keto-1:4-dihydro-2:3-pentamethylenequinoline.*—5-Bromoanthranilic acid (2.16 g.) and *cyclo*heptanone (1.12 g.) were heated in an oil bath at 240° for 3 hours. The product after usual purification was repeatedly crystallised from ethanol in brownish needles, m.p. 340°, undepressed by admixture with the product obtained by the direct bromination of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline. (Found: Br, 27.7. Calc. for $C_{14}H_{14}ONBr$: Br, 27.49%).

*Synthesis of 8-Bromo-4-keto-1:4-dihydro-2:3-pentamethylenequinoline.*—3-Bromoanthranilic acid (2.16 g.) and *cyclo*heptanone (1.12 g.) were heated in an oil bath at 210-20° for 2 hours, the temperature being gradually raised. The solid after the usual purification was crystallised from ethanol in colorless needles, m.p. 329°, undepressed by admixture with the product obtained by direct bromination of 4-keto-1:4 dihydro-2:3-pentamethylenequinoline. (Found : Br, 27.68. Calc. for $C_{14}H_{14}ONBr$ : Br, 27.49%).

*6:8-Dibromo-4-keto-1:4-dihydro-2:3-pentamethylenequinoline.*—To a solution of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline (2.13 g.) in glacial acetic acid (12 c.c.) with a trace of iodine, cooled to 5°, was added slowly a 20% solution of bromine in glacial acetic acid (16 c.c.). After keeping the mixture in an ice bath for 24 hours, it was poured into water and the solid was filtered, washed, dried, and crystallised from absolute ethanol in light brown needles, m.p. 325°, yield 3.0 g. It was identified as 6-8-dibromo derivative by mixed m.p. with the authentic specimen obtained from 3:5-dibromoanthranilic acid and *cyclo*heptanone. The same product can also be obtained by the bromination of either 6-bromo or 8-bromo derivative. (Found: Br. 43.00. Calc. for $C_{14}H_{13}ONBr_2$: Br, 43.24%).

*Synthesis of 6:8-Dibromo-4-keto-1:4-dihydro-2:3-pentamethylenequinoline.*—A mixture of 3:5-dibromoanthranilic acid (2.63 g.) and *cyclo*heptanone (1.12 g.) was heated in an oil bath at 180° for 1 hour and then at 230° for further one hour. The pasty mass was triturated with petrol b.p. 40-50°) and then with ether. The residue was crystallised from 90% ethanol in light brown needles, m.p. 325°, undepressed by admixture with the dibromo derivative obtained by the direct bromination of the original product. (Found: Br, 43.45. Calc. for $C_{14}O_{13}ONBr_2$: Br, 43.24%).

*6-&8-Nitro-4-keto-1:4-dihydro-2:3-pentamethylenequinolines.*—A solution of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline (2.13 g.) in $H_2SO_4$ (*d* 1.89, 15 c.c.) was cooled to —5°. A mixture

of $HNO_3$ (*d* 1.49, 0.42 c.c.) and $H_2SO_4$ (conc., 5 c.c.), cooled to $-5°$, was added to the above cooled solution with constant stirring. After keeping the mixture in an ice bath for 12 hours it was poured in ice water. The precipitated solid was filtered, washed, dried and crystallised from ethanol in pale yellow plates, m.p. 355°, yield 0. 85 g. This was proved to be 8-nitro derivative on comparison with the authentic specimen prepared from 3-nitroanthranilic acid and *cyclo*heptanone. (Found : N, 10.70. $C_{14}H_{14}O_3N_2$ requires N, 10.86%).

The yellowish mother liquor on concentration and cooling deposited a solid, which after several crystallisations from ethanol afforded orange-yellow microcrystals, m.p. 277°. This was shown to be the 6-nitro derivative on comparison with the authentic specimen. (Found: N, 10.62. $C_{14}H_{14}O_3N_2$ requires N, 10.86%).

*Synthesis of* 6-*Nitro*-4-*keto*-1:4-*dihydro*-2:3-*pentamethylenequinoline*.—A mixture of 5-nitroanthranilic acid (3.64 g.) and *cyclo*heptanone (2.24 g.) was heated at 120-30° for 2 hours and then at 230° for further 3 hours. The product was washed with benzene to remove the impurities and then crystallised from 90% ethanol in orange-yellow microcrystals, m.p. 277°. The m.p. showed no depression when mixed with the second isomer obtained by the direct nitration of the 4-keto-1:4-dihydro-2:3-pentamethylenequinoline. (Found: N, 11.0. Calc. for $C_{14}H_{14}O_3N_2$: N, 10.86%).

*Synthesis of* 8-*Nitro*-4-*keto*-1:4-*dihydro*-2:3-*pentamethylenequinoline*.—A mixture of 3-nitroanthranilic acid (3.64 g.) and *cyclo*heptanone (2.24 g.) was heated at 120-30° for 2 hours and then at 230° for further 2 hours. The product was crystallised from ethanol in pale yellow plates, m.p. 355°, undepressed by admixture with the product obtained by direct nitration of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline. (Found: N, 10.7. Calc. for $C_{14}H_{14}O_3N_2$: N, 10.86%.)

6:8-*Dinitro*-4-*keto*-1:4-*dihydro*-2:3-*pentamethylenequinoline*.—A nitrating mixture of $HNO_3$ (*d* 1.49, 0.84 c.c) and $H_2SO_4$ (conc., 5 c.c), cooled to $-5°$, was slowly added to the cooled solution of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline (2.13 g.) in $H_2SO_4$ (*d* 1.89, 15 c.c.). After keeping the mixture in an ice bath for 14 hours, it was poured on crushed ice. The precipitated solid was finally crystallised from ethanol in pale yellow plates, yield 2.0 g., m.p. 357°, undepressed on admixture with the authentic specimen. The same product was also obtained by direct nitration of either 6-nitro or 8-nitro derivative. (Found: N, 13.62. $C_{14}H_{13}O_5N_3$ requires N, 13.90%).

*Synthesis of* 6:8-*Dinitro*-4-*keto*-1:4-*dihydro*-2:3-*pentamethylenequinoline*.—A mixture of 3:5-dinitroanthranilic acid (4.5 g.) and *cyclo*heptanone (2.24 g.) was heated in an oil bath at 130-40° for 2 hours and further at 220-30° for 2 hours. The product on crystallisation from ethanol furnished pale yellow plates, m.p. 357°, undepressed by admixture with the dinitro compound obtained by nitration of 4-keto-1:4-dihydro-2:3-pentamethylenequinoline. (Found: N; 13.58. Calc. for $C_{14}H_{13}O_5N_3$: N, 13.9%).

1-o-*Carboxyanilino*-$\Delta^{1:2}$-*cyclooctene*.—A mixture of anthranilic acid (5 g.) and *cyclo*octanone (5 g.) was heated in an oil bath at 120° for 3 hours. The solid after washing with little benzene to remove the impurities was crystallised from benzene in colorless, small prisms, m.p. 125°, yield 5.7 g. (Found : C, 73.21; H, 7.4. $C_{15}H_{19}O_2N$ requires C, 73.40; H, 7.7%).

4-*Keto*-1:4-*dihydro*-2:3-*hexamethylenequinoline*.—The above anil was heated in an oil bath at 220° for 2½ hours. The solid after being treated with a dilute solution of sodium bicarbonate was crystallised from benzene in colorless, small plates, m.p. 323°. (Found: C, 78.6; H, 7.8; N, 5.87. $C_{15}H_{17}ON$ requires C, 79.2; H, 7.4; N, 6.16%).

TABLE I

[Q = 4-keto-1:4-dihydro-2:3-hexamethylenequinoline]

| No. | Compounds. | M.P. | *Cryst shape. | Formula. | Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | 6-Bromo-Q | 340° | Colorless needles | $C_{15}H_{16}ONBr$ | Br: 25.96% | 26.14% |
| 2. | 8-Bromo-Q | 305° | Light brown needles | $C_{15}H_{16}ONBr$ | Br: 26.00 | 26.14 |
| 3. | 6:8-Dibromo-Q | 305° | Brown needles | $C_{15}H_{15}ONBr_2$ | Br: 41.24 | 41.55 |
| 4. | 6-Nitro-Q | 348° | Pale yellow microcrystals | $C_{15}H_{16}O_3N_2$ | N: 10.06 | 10.29 |
| 5. | 8-Nitro-Q | 352° | Dark orange microcrystals | $C_{15}H_{16}O_3N_2$ | N: 10.09 | 10.29 |
| 6. | 6:8-Dinitro-Q | 356° | Do | $C_{15}H_{15}O_5N_3$ | N: 13.40 | 13.22 |

* All crystallised from ethanol, the last compound (6) from absolute ethanol.

N.B. The authentic specimens of compounds 1, 2 and 3 were synthesised by condensing 5-bromo-, 3-bromo- and 3:5-dibromo-anthranilic acids with *cyclo*octanone and the compounds 4, 5 and 6 were synthesised by condensing 5-nitro-, 3-nitro- and 3:5-dinitro-anthranilic acids with *cyclo*octanone by the method described above for comparison.

TABLE II

[A = 2-methyl-1:2:3:4-tetrahydroacridone]

| No. | Compound. | M.P. | *Cryst. form. | Mol. formula. | Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | 7-Bromo-A | 327° | Yellowish needles | $C_{14}H_{14}ONBr$ | Br: 27.15% | 27.39% |
| 2. | 9-Bromo-A | 342° | **Colorless needles | $C_{14}H_{14}ONBr$ | Br: 27.19 | 27.39 |
| 3. | 7:9-Dibromo-A | 315° | Pale yellow needles | $C_{14}H_{13}ONBr_2$ | Br: 42.93 | 43.12 |
| 4. | 7-Nitro-A | 310° | **Canary yellow plates | $C_{14}H_{14}O_3N_2$ | N: 10.60 | 10.85 |
| 5. | 9-Nitro-A | 350° | Pale yellow needles | $C_{14}H_{14}O_3N_2$ | N: 10.66 | 10.85 |
| 6. | 7:9-Dinitro-A | 340° | **Yellowish orange microcrystals | $C_{14}H_{13}O_5N_3$ | N: 14.10 | 14.33 |

* From ethanol.

** From absolute ethanol.

N.B. The authentic specimens of compounds 1, 2 and 3 were synthesised by condensing 5-bromo-, 3-bromo- and 3:5-dibromo-anthranilic acids with 3-methyl*cyclo*hexanone and compounds 4,5 and 6 by condensing 5-nitro-, 3-nitro- and 3:5-dinitro-anthranilic acids with 3-methyl*cyclo*hexanone by the method described above.

The bromo and nitro derivatives obtained by the monobrominaion, dibromination, mononitration, and dinitration of 4-keto-1:4-dihydro-2:3-hexamethylenequinolines are shown in Table I. Those of 2-methyl-1:2:3:4-tetrahydroacridone are listed in Table II. Their constitutions were proved by mixed m.p. with the authentic specimens.

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# SPECTROPHOTOMETRIC STUDY OF FERRIC—*p*-AMINOSALICYLATE COMPLEX

BY REBATI CHARAN DAS AND S. ADITYA

The nature of $Fe^{3+}$—*p*-aminosalicylate complex has been studied spectrophotometrically. At *p*H 2.5 the complex contains one atom of Fe(III) and one molecule of *p*-aminosalicylic acid. The association constant of the complex has been determined at ionic strengths 0.02, 0.05, 0.1, and 0.2*M*. By empirical extrapolation the thermodynamic association constant has been found to be $3.72\times10^4$ at $30^\circ \pm 1^\circ$.

Phenols, phenolic acids and aminophenols form intense violet-coloured complexes with trivalent iron. The nature of some of these complexes has been studied by *p*H titrations. Only a few of these have been studied, however, by spectrophotometry. Ferric—salicylate complex was studied by Babko (*Zhur. Obscher. Khim.*, 1948, **18,** 1617) and ferric—sulphosalicylate complex by Anderson *et al.* (*J. Amer. Chem. Soc.*, 1948, **70,** 1195). Both the workers report the formation of a complex with metal ion to ligand in the molecular ratio of 1 :1 at lower *p*H. At higher *p*H, the colour of the solution changes, indicating formation of complexes with metal to ligand in molecular ratios of 1 : 2 and 1 : 3. Spectrophotometric method cannot, however, be used at high *p*H on account of hydrolysis of Fe(III) to a colloidal condition.

Ferric ion also forms a violet complex with *p*-aminosalicylic acid, sodium salt of which has been used more recently for colorimetric estimation of iron (Mukherjee, *Anal. Chim. Acta*, 1955, **13,** 273) and gravimetric estimation of copper, mercury, bismuth, silver, and cerium (*Chem. Abst.*, 1950, 11877; Suranova and Olenovich, *Trudi Odesk Univ., Sbornik. Khim. Fak*, 1953, **3,** 71). Recently Agren (*Acta Chem. Scand.*, 1954, **8,** 1059) has studied the complex formation between $Fe^{3+}$ and some phenolic acids. He investigated the nature of *p*-aminosalicylic acid and its Fe (III) complex photometrically and potentiometrically. The photometric determination was done only at one ionic strength, namely in 3*M* sodium perchlorate medium. In the present work a detailed study of the ferric—*p*-aminosalicylate complex has been done spectrophotometrically. The stability constant has been determined at different ionic strengths so as to get an idea of the thermodynamic stability constant.

## EXPERIMENTAL

Ferric perchlorate was prepared by dissolving the reagent grade iron powder in dilute perchloric acid (E. Merck, G. R.) and oxidising the ferrous perchlorate formed with hydrogen peroxide. The absence of ferrous ion in solution was tested by *o*-phenanthroline. The *p*H of the stock solution was found to be 1.78. Iron was estimated iodometrically (Vogel, "Text Book of Quantitative Inorganic Analysis", 1946, 2nd ed., p. 356; Patnaik *et al.*, *Curr. Sci.*, 1956, **25,** 55).

Rhodia's reagent grade sodium salt of *p*-aminosalicylic acid was used as the ligand. The sample was purified by crystallisation and dried in a vacuum desiccator. The salt was found more stable than the acid in solution (cf. Agren, *Farm. Revy*, 1955, **54,** 225).

Sodium perchlorate of B.D.H. pure quality was used to maintain the ionic strength. Perchloric acid and sodium hydroxide used were of E. Merck's G. R. quality. The solutions were prepared in double distilled water.

For the measurement of optical density a Hilger-Watt "UVISPEK" spectrophotometer of type H 700-303 was used. In absence of any arrangement for thermostating in the instrument used, all measurements were done at room temperature ($30^\circ\pm1^\circ$).

The absorption measurements were taken in clean quartz cells of 1 cm path length. To avoid any possible error, caused by non-matching, readings were taken with cells interchanged. Each reading was taken with two different solutions. The slit width was kept fixed at 0.01 mm. This corresponds to a band width of 5 Å.

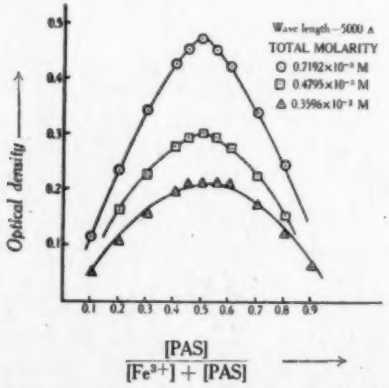
The *p*H of the solutions was measured with a Marconi *p*H meter (model TF 511 D). In the present case, *p*H was adjusted at 2.5 by mixing the reactants at definite proportions and making the volume to 100 c.c. A known volume of the above solution was taken and its *p*H measured. The acid or alkali as required were added dropwise to adjust the *p*H at 2.5. Knowing the actual number of drops of acid or alkali required to adjust the *p*H, the same solution was prepared and the required number of drops of acid or alkali added before dilution. Each solution was prepared in duplicate with adjusted *p*H, and its absorbance measured within a few hours of its preparation.

## DISCUSSION

Although ferric perchlorate and sodium salt of *p*-aminosalicylic acid individually do not exhibit any absorption in the wave length region used, a solution containing both has an absorption maximum at 500 mμ. To ascertain the stability of the colour developed by the mixed solution of the two, its optical density was measured for a few hours at an interval of half an hour. Intensity of the colour developed did not change in 4 to 5 hours.

*Molecular Composition of the Complex.*—The molecular composition of the complex at *p*H 2.5 was determined by using Job's method of continued variation (Job, *Ann. Chim.*, 1928, *x*, **9**, 113 ; 1936, *xi*, **6**, 97 ; Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437). The absorption spectra of solutions containing different proportions of ferric perchlorate and P.A.S., adjusted at *p*H 2.5, were run over a range of 400-600 mμ. The total molarities of the solutions were kept constant ; in the present case at $0.4795\times10^{-3}M$, $0.7192\times10^{-3}M$ and $0.3596\times10^{-3}M$. The figure gives the Job's curve at 500 mμ. The same also has been drawn at wave lengths 400 mμ to 600 mμ at an interval of 20 mμ. In the curves the positions of the maxima suggest the presence of 1 : 1 complex at the *p*H concerned. That the peaks of all the curves remain the same indicates the probable presence of only one complex in the solution.

FIG. 1

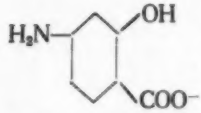



*Extinction Coefficients.*—Ferric perchlorate and P.A.S. were mixed in ratios of 1 : 9, 1 : 10, 1 : 12, etc. so that the latter always existed in excess, as any excess of the former had an oxidising influence. The *p*H of the solutions was adjusted at 2.5, and absorbance measured at 500 mμ.

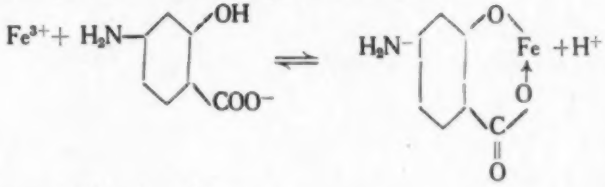
On assuming that the complex formation was complete, the concentration of the complex was taken to be equal to that of ferric perchlorate, and the extinction coefficient calculated from Beer's law. The mean extinction coefficient value of the complex at 500 mμ was found to be 1675 ± 7°.

*Equilibrium Constant of the Complex.*—Absorption measurements of the mixed solutions with *p*H were made for the quantitative determination of the stability constant. The ionic strengths of the solutions were taken to be equal to the concentrations of sodium perchlorate as it was always present in large quantities as compared to other components.

From the continued variation curve it is apparent that the complex is formed by the combination of $Fe^{3+}$ and P.A.S. in molecular ratio of 1 : 1. Since the dissociation constant of the -COOH group in the ligand is $10^{-4.08}$ ("Stability Constants. Part I", the Chemical Society, London, special publication No. 6, p. 57) at *p*H 2.5, the acid will exist to a large extent in the dissociated form as



The equilibrium between $Fe^{3+}$ and P.A.S. may be written as



The formation constant $K'$ can be written as

$$K' = \frac{[FeR]\,[H^+]}{[Fe^{3+}]\,[HR^-]}$$

or when $[H^+]$ is fixed, we have $\frac{[FeR]}{[Fe^{3+}]\,[HR^-]}$ to be constant. $[HR^-]$ may be taken as $\{[HR^-]_{total} - [HR^-]_{bound}\}$. If, however, one takes into account the fact that the ligand may not exist totally as $[HR^-]$, it can be shown that

$$\{[H_2R]_{total} - [FeR]\} = [HR^-]\left\{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right\}$$ where $K_1$ and $K_2$ are dissociation constants for $H_2R \rightleftharpoons H^+ + HR^-$ and $HR \rightleftharpoons H^+ + R^{2-}$ respectively. So

$$\frac{[FeR]}{[Fe^{3+}]_{free}\{[H_2R]_{Total} - [FeR]\}}$$

is constant at a constant *p*H. In our calculation of the association constant, we have used this expression. The various terms in the expression are obtained in the following way. [FeR] is calculated from the measured optical density of the solution containing the metal ion and the ligand, using Beer's law, the extinction coefficient of the complex species having been known. The total concentrations of the metal ion and the ligand are known and, hence the concentration terms in the denominator. Thus, all the terms being known, the association constant is calculated.

The results recorded in Table I show one typical reading for each ionic strength. At each ionic strength about ten sets of readings with different amounts of ligand and metal ion have been taken. The average value of the association constant with standard deviations has been noted. The

association constants are $(3.06\pm0.06)\times10^4$, $(2.56\pm0.12)\times10^4$, $(2.37\pm0.12)\times10^4$ and $(2.21\pm0.11)\times10^4$ at ionic strengths 0.02, 0.05, 0.1 and 0.2 respectively. An attempt has been made to get the thermodynamic association constant by extrapolation to zero ionic strength. Since none of the extrapolations, either log $K$ against $\mu$ (ionic strength) or log $K$ against $\sqrt{\mu}$ give a linear extrapolation, the value of log $K$ at $\mu=0$ has been obtained by both the methods of extrapolation. The average value is $3.72\times10^4$.

TABLE I

| Molarity ($\times10^4$) of $Fe(ClO_4)_3$. | Molarity ($\times10^4$) of P.A.S. | Inoic strength. | Opitcal density. | $K\times10^{-4}$ | No of readings taken with diff. conc. of reactants. | Average $K\times10^{-4}$. |
|---|---|---|---|---|---|---|
| 2.877 | 2.397 | 0.02 | 0.3059 | 3.05 | 9 | $3.06\pm0.06$ |
| 4.795 | 4.795 | 0.05 | 0.6077 | 2.66 | 9 | $2.56\pm0.12$ |
| 3.356 | 2.397 | 0.10 | 0.3105 | 2.27 | 9 | $2.37\pm0.12$ |
| 2.877 | 1.918 | 0.20 | 0.2395 | 2.02 | 9 | $2.21\pm0.11$ |

As mentioned earlier, Agren (*loc. cit.*) made a quantitative study of the $Fe^{3+}$—P.A.S. system. He kept the ionic strength of the medium fixed at 3*M*. So a quantitative comparison of our results with his is not possible. A semiquantitative comparison can, however, be made. Agren found the violet complex to be composed of one atom of iron and one molecule of P.A.S. In our experiments at *p*H 2.5, the continued variation curve at different wave lengths indicates the complex to possess a molecular ratio of 1 : 1. It may be mentioned here that the species FeRH would also give a maximum in Job's curve at 1 : 1. But the species FeRH is probably not present, or even if it is there, the concentration is negligibly small because the dissociation of the $H_3R^+$ will be almost complete at *p*H 2.5 for $pK_{a_1}=2.0\%$ (*loc. cit.*). So we assume that the complex is only FeR. To get an idea as to how far the association constant in the present determination and that of Agren agree, we have calculated the value of the

$$\frac{[Fe^{3+}]\ [R^{2-}]}{[FeR]}$$

from our results. Using the different stages of equilibrium of the dissociation of the ligand ($pK_{a_1}=2.08$, $pK_1=4.08$, $pK_2=13.74$; *loc. cit.*) it can be easily shown that the present association constant is related to

$$\frac{[Fe^{3+}]\ [R^{2-}]}{[FeR]}$$

as in the equations :

$$\frac{1}{K}=\frac{[Fe^{3+}]\left\{[H_2R]_T-[FeR]\right\}}{[FeR]}=\frac{[Fe^{3+}]\ [R^{2-}]\left\{\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1\right\}}{[FeR]} \qquad \ldots\ (1)$$

when the dissociation of the -COOH and -OH groups of the ligand are considered ; or

$$\frac{1}{K}=\frac{[Fe^{3+}]\ [R^{2-}]}{[FeR]}\left\{\frac{[H^+]^3}{K_{a_1}K_1K_2}+\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1\right\} \qquad \ldots\ (2)$$

when the dissociation of $-NH_3^+$, $-COOH$ and $-OH$ groups are considered. From our measurements, the value of

$$\frac{[Fe^{3+}]\ [R^{2-}]}{[FeR]}$$

at ionic strength 0.2 *M* comes out to be $0.76 \times 10^{-17}$ and $0.43 \times 10^{-17}$ on the basis of equations (1) and (2) respectively. The value reported by Agren is $1.07 \times 10^{-17}$ at ionic strength 3 *M*. The effect of increase in ionic strength has a tendency to increase the dissociation constant by decreasing the activity of the ionic species. So qualitatively the trend is correct, although it is very difficult to suggest how far quantitatively such high ionic strength of the medium should increase the value of dissociation constant. However, the order of agreement is satisfying.

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# 3-HYDROXY-1-*p*-SULPHONATOPHENYL-3-PHENYLTRIAZINE AS AN INDIRECT SPECTROPHOTOMETRIC REAGENT FOR FLUORIDE

BY MISS SUSHILA MEHRA AND N. C. SOGANI

The fading of ferric—3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine, a bluish black complex with fluoride ions, is made the basis for the indirect spectrophotometric determination of fluoride in the concentration range of 0.5 to 40 p.p.m. Phosphate, borate, citrate, tartrate, oxalate, and cyanide interfere; other common anions do not. This method can be applied for determining fluoride in water samples.

Fluoride determinations have become increasingly important in recent years, and several spectrophotometric methods are described in the literature. As fluoride does not form coloured complexes, only indirect spectrophotometric methods have been proposed to date. These procedures are based on measuring the bleaching of some coloured metal complex by the formation of stable complex between the metal ion and fluoride.

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine develops an intense bluish black, water-soluble colour with Fe(III) (Gupta and Sogani, this *Journal*, 1960, **37**, 97). In the present investigation the fading of this colour with fluoride ions is made the basis for the indirect spectrophotometric determination of fluoride in micro quantities. The fading is directly proportional to the amount of ferric ions withdrawn from the system in the formation of more stable ferric fluoride complex. The following equilibria exist :

$$Fe^{3+} + 3\,RH \rightleftharpoons FeR_3 + 3\,H^+ \quad \ldots\ \ldots \quad (i)$$

$$FeR_3 + 6\,F^- \rightleftharpoons [FeF_6]^{3-} + 3\,R^- \quad \ldots\ \ldots \quad (ii)$$

(RH = reagent)

The extent to which the reaction proceeds depends on the relative stabilities of $FeR_3$ and $[FeF_6]^{3-}$ complexes in the reaction mixture.

## EXPERIMENTAL

*Standard Sodium Fluoride Solution.*—Pure sodium fluoride (5.0 g.) was dissolved in distilled water and the volume made to 500 c.c. Fluoride content was determined gravimetrically by lead chlorofluoride method (Scott, "Standard Methods of Chemical Analysis", 1939, p. 405) and was diluted so as to contain 80 p.p.m. of fluoride.

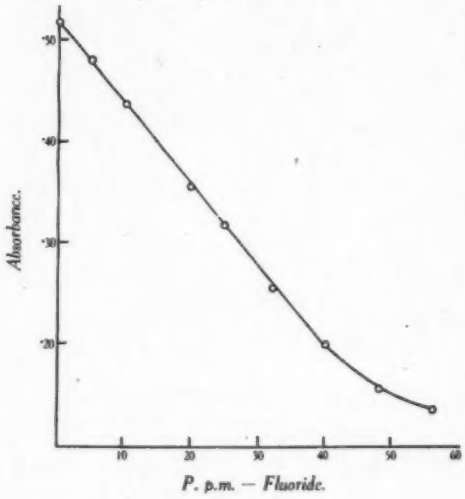
Standard ferric chloride, reagent and buffer solutions, and instruments were the same as described earlier (*loc. cit.*).

*Calibration Curve.*—In a volume of 50 c.c., 10 c.c. of the standard ferric chloride solution ($M\times10^{-3}$) was found to produce a colour, readable by the photoelectric colorimeter. Required amounts of 10% HCl (v/v) and 10% sodium acetate (w/v) solution were added so as to bring the *p*H to $\sim$ 3.0 after necessary dilution. It was followed by 10 c.c. of 0.4% aqueous reagent

solution. Different volumes of the standard fluoride solution were added in a series of solutions, prepared as described above. The volume was then made up to the mark and absorbance was measured at 650 mμ, taking water in the reference cell.

Fig. 1 shows the effect of increasing fluoride concentration on fading of bluish black iron complex. The amount of iron withdrawn from reaction is proportional to the concentration of fluoride in the range from 0.5 to 40 p.p.m. of fluoride. After 40 p.p.m. of fluoride the fading of colour is less than the amount of fluoride added. Ions forming stable complexes with Fe(III) like phosphate, oxalate, citrate, tartrate, cyanide, etc., or with fluoride ion, like borate, interfere; common anions like chloride, sulphate, nitrate, acetate, etc. do not interfere in the determination.

FIG. 1




*Effect of Time.*—An experiment was performed to find out the time taken for the establishment of the equilibrium in the reaction (*ii*). A sample was prepared as described above and the absorbance measured at different intervals of time. There was no change in the absorbance with time. Hence the equilibrium is established almost instantaneously.

*Determination of Fluoride in Water.*—Boruff and Abbott have reported (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5,** 236) that water containing small quantities of fluorides, when made alkaline to phenolphthalien or litmus, can be concentrated without loss of fluorine. Most natural waters do not contain enough phosphate or borate in the volume used for determination of fluoride to interfere with the accuracy of the method.

A 100 c.c. sample of water was taken in a shallow beaker, made alkaline to phenolphthalein, and concentrated to 25 to 30 c.c. by gentle heating. The quantity of the sample to be taken depends upon the fluoride content present, which should be within 0.025 to 2 mg. After cooling, the *p*H was adjusted to about 3.0 by adding 10% HCl (v/v). In a 50 c.c. volumetric flask standard ferric chloride, buffer solutions, and reagent solution were added, as described earlier, followed by the sample of water prepared, as described above. After making up the volume to the mark, the absorbance was measured at 650 mμ, taking water as a reference solution. The amount of fluoride was read from the calibration curve.

## DISCUSSION

Fluoride is determined by its fading action on the colour of ferric thiocyanate (Foster, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5,** 234), acetylacetone (Armstrong, *ibid.*, p. 300), 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Fahey, *ibid*, 1939, **11,** 362), sulphosalicylic acid (Monnier *et al.*, *Helv. Chim. Acta*, 1946, **29,** 521), and salicylic acid (Kortum and Seller, *Angew. Chem.*, 1947, **A 59,** 159). The complexes of zirconium and thorium with hydroxyanthraquinones have been successfully used (Bumstead and Wells, *Anal. Chem.*, 1952, **24,** 1595; Talvite, *Ind. Eng. Chem., Anal.*

*Ed.*, 1943, **15,** 620; Nommik, *Acta Polytech., Chem. Met. Ser.*, 1953, **3,** vii, 121). The decoloration of aluminium—chromeazurol (McNulty and Woolard, *Anal. Chim. Acta*, 1955, **13,** 134) and eriochromecyanine (McNulty *et al.*, *ibid.*, 1956, **14,** 368) complexes by fluoride have been studied. A comparative study of some of the important methods has been made by Kojima *et al.* (*Japan Analyst*, 1955, **4,** 607).

3-Hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine introduces one more compound in the list of good reagents for the indirect spectrophotometric determination of fluoride. No claim for its superiority over other reagents is made.

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# GUANYLALKYLUREAS AND THEIR METALLIC COMPLEXES. PART V. PALLADIUM COMPLEXES*

By R. L. Dutta, Bimanesh Sur and Nihar Ranjan Sengupta

Complex compounds of palladium (II) with guanylalkylureas have been prepared and their properties studied. The complex palladium *bis*-guanylalkylurea bases and their salts are all pale cream in colour. The equivalent conductance measurements indicate the bivalent nature of the complex cation. The compounds are all diamagnetic, suggesting a planar structure with $dsp^2$ hybrid bonds.

The cream-coloured palladium *bis*-guanylalkylurea thiocyanates undergo rearrangement in presence of dilute acid to form ruby-red palladium *bis*-guanylalkylurea-palladothiocyanate.

Palladium(II) complexes of unsubstituted guanylurea and of phenylguanylurea have been studied by Rây and Bandopadhyay (this *Journal*, 1952, **29**, 865). A series of guanylalkylureas have recently been prepared, and comprehensive studies of the copper and nickel complexes of these ligands recorded in the earlier parts of this series (Dutta and Rây, this *Journal*, 1959, **36**, 499, 567, 576). The present work was undertaken with a view to making a comparative study of the behaviour of nickel(II) and palladium(II). It deals with the preparation and properties of the paladium (II) complexes of guanylmethyl-, -ethyl-, -butyl$^n$-, -butyl$^i$-, -amyl$^i$- and -hexyl$^n$ureas.

The compounds can be represented as :

I. $[Pd\ (Gau)_2]$ or $[Pd\ (Gau)_2].\ 0.5H_2O$ where GauH=a molecule of guanylalkylurea.
II. $[Pd\ (GauH)_2]\ X_2.xH_2O$ where X=Cl, $\frac{1}{2}SO_4$, $NO_3$, SCN, etc.
III. $[Pd\ (GauH)_2]\ [Pd\ (SCN)_4]$

The complex palladium (II)-*bis*-guanylalkylurea sulphates have been prepared as sparingly soluble products by the addition of a solution of sodium chloropalladite to that of the guanylalkylurea sulphate in neutral or faintly ammoniacal medium.

$$(GauH)_2H_2SO_4 + Na_2PdCl_4 \rightarrow [Pd(GauH)_2]\ SO_4 + 2\ HCl + 2\ NaCl.$$

The complex chlorides were prepared either by the action of barium chloride on the complex sulphate or by neutralising the complex base with hydrochloric acid. The solubility of the chloride salts in water decreases with increase in the chain length of the substituent at the urea end of the molecule, whereas that in alcohol increases. Several salts of the complex bases, namely, iodide, nitrate and thiocyanate, were obtained as silky, cream-coloured crystalline precipitates by double decomposition between the complex chloride and the appropriate alkali metal salt in aqueous or in aqueous alcoholic solution. The complex palladium guanylethylurea bases and those of the higher guanylureas were prepared as water-insoluble products by digesting a solution of sodium chloropalladite and the guanylalkylurea concerned in presence of sodium hydroxide. It has not been possible, however, to isolate the complex palladium guanylmethylurea base due to its extreme solubility in water. The complex bases in the solid state conform to the composition of anhydro-bases or to hemi-hydrates. These liberate ammonia from ammonium salts and react alkaline to litmus.

Complex palladium-*bis*-guanylalkylurea thiocyanates on treatment with dilute acid solution deposited a ruby-red insoluble mass, characterised as the palladium-*bis*-guanylalkylurea palladothiocyanate.

* A preliminary note appeared in *Science & Culture*, 1959, **25**, 381.

$$2\,[Pd\ GauH)_2]\ (SCN)_2 + 2\,HCl \rightarrow [Pd\ (GauH)_2]\ [Pd\ (SCN)_4] + 2\,GauH.\,HCl$$

In this respect, the complex palladium-guanylurea thiocyanates resemble their biguanide analogues (Rây and Ghosh, this *Journal*, 1943, **20**, 19).

The complexes are all stable in boiling water or alcohol. The equivalent conductances of the chloride salts of the palladium guanylmethylurea and of palladium guanylethylurea in water are in fair agreement with those of bi-univalent electrolytes. The compounds are all diamagnetic, indicating a planar structure characteristic of penetration complexes of palladium with $dsp^2$ bonds. These compounds show a close similarity to the corresponding nickel complexes in respect of composition, properties and also magnetic characteristics. Like nickel, palladium (II) also does not form any *mono*-guanylalkylurea complex. Nickel (II) and palladium (II) thus present a marked difference from copper (II), so far as their behaviour towards biguanides and guanylureas is concerned.

## EXPERIMENTAL

### *Complex Compounds of Palladium with Guanylmethylurea*

*Palladium*-bis-*guanylmethylurea Sulphate.*—An aqueous solution of sodium chloropalladite ($PdCl_2$, 0.5 g.) was added to that of guanylmethylurea sulphate (1.3 g.) (total volume 80 c.c.) and cooled in an ice bath. The complex palladium sulphate separating as a fine, silky, pale cream, crystalline mass was filtered, washed with water and little ethanol, and dried in air. {Found : Pd, 23.01; $SO_4$, 20.65; N, 23.65; $H_2O$ (by loss at 110°), 7.52. $[Pd\ (C_3H_8N_4O)_2]\ SO_4.2H_2O$ requires Pd, 22.75; $SO_4$, 20.47; N,28.88; $H_2O$, 7.67%}. $\chi_g = -0.15 \times 10^{-6}$.

*Chloride.*—Complex palladium sulphate (2 g.), obtained as above, was suspended in water (30 c.c.) and digested on a water bath with barium chloride (1 g. in 30 c.c.) solution for about an hour. The mixture was then filtered, the filtrate concentrated (25 c.c.) on the water bath and left in the frigidiare overnight. The pale cream-coloured crystals separating were filtered, washed first with cold water, then with ethanol, and finally dried in air. {Found : Pd, 24.24; Cl, 16.23; $H_2O$ (by loss at 110°), 8.13. $[Pd(C_3H_8N_4O)_2]\ Cl_2.2H_2O$ requires Pd, 24.03; Cl, 16.0; $H_2O$, 8.10%}.

The *nitrate* was obtained as a precipitate by the interaction of the complex palladium chloride with potassium nitrate in aqueous solution. {Found : Pd, 21.20; $H_2O$ (by loss at 110°), 8.35. $[Pd(C_3H_8N_4O)_2]\ (NO_3)_2,\ 2.5H_2O$ requires Pd, 21.09; $H_2O$, 8.89%}.

The *iodide*, obtained by the action of KI on the complex chloride, is insoluble in water but readily soluble in ethanol. {Found : Pd, 17.20; $H_2O$ (by loss at 110°), 5.92. $[Pd\ (C_3H_8N_4O)_2]I_2$, $2H_2O$ requires Pd, 17.01; $H_2O$, 5.74%}.

The *thiocyanate*, obtained by the action of KSCN on the complex chloride, was washed with ice-cold water. It is readily soluble in water and in ethanol. {Found : Pd, 22.70; SCN, 24.35 ; $H_2O$, 3.96. $[Pd\ (C_3H_8N_4O)_2]\ (SCN)_2.H_2O$ requires Pd, 22.65; SCN, 24.62; $H_2O$, 3.82%}.

*Palladium*-bis-*guanylmethylurea Palladothiocyanate.*—The complex palladium thiocyanate (0.5 g.), obtained as above, was taken in water (40 c.c.), treated with a few drops of HCl (3 *N*) and digested on a water bath for about 1½ hours when ruby-red, silky crystals separated out. These were filtered, washed with water and ethanol, and then dried in air. The same compound was also obtained by the interaction of palladium-*bis*-guanylmethylurea chloride and potassium palladothiocyanate. {Found : Pd, 31.69; SCN, 34.88. $[Pd\ (C_3H_8N_4O)_2]\ [Pd\ (SCN)_4]$ requires Pd, 31.56; SCN, 34.31%}.

### *Complex Compounds of Palladium with Guanylethylurea*

*Palladium* bis-*Guanylethylurea.*—A mixture of sodium chloropalladite (1 *M*) and guanylethylurea sulphate (1.5 *M*) was made alkaline with NaOH. A clear solution was obtained, which immediately afterwards deposited a very fine, silky crystalline precipitate. This was filtered. It was washed with water and ethanol, and then dried over KOH. {Found : Pd, 29.02; N, 30.35. $[Pd\ (C_4H_9N_4O)_2]$ requires Pd, 29.23; N, 30.69%}.

The following compounds were obtained as described in the case of guanylmethylurea.

*Sulphate :* {Found : Pd, 20.47; $SO_4$, 18.26; N, 21.46; $H_2O$ (by loss at 110°), 10.85. $[Pd\ (C_4H_{10}N_4O)_2]SO_4.3H_2O$ requires Pd, 20.63; $SO_4$, 18.56; N, 21.66; $H_2O$, 10.44%}. $\chi_g = -0.12\times10^{-6}$.

*Nitrate :* {Found: Pd, 20.98, $H_2O$, 1.76. $[Pd\ (C_4H_{10}N_4O)_2].(NO_3)_2$. 0.5 $H_2O$ requires Pd, 21.34; $H_2O$, 1.80%}.

*Chloride :* {Found : Pd, 22.25 ; Cl, 14.78 ; $H_2O$ (by loss at 110°), 9.72. $[Pd\ (C_4H_{10}N_4O)_2]$-$Cl_2.2.5H_2O$ requires Pd, 22.09 ; Cl, 14.70 ; $H_2O$, 9.3%}.

*Iodide :* {Pd 16.43 ; $H_2O$, 5.48. $[Pd\ (C_4H_{10}N_4O)_2]I_2.2H_2O$ requires Pd,16.23 ; $H_2O$, 5.48%}.

*Thiocyanate :* {Found : Pd, 21.09 ; SCN, 23.54. $[Pd(C_4H_{10}N_4O)_2]\ (SCN)_2.H_2O$ requires Pd, 21.29 ; SCN, 23.15%}.

*Palladium*-bis-*guanylethylurea Palladothiocyanate :* {Found : Pd, 30.18 ; SCN, 33.05. $[Pd$-$(C_4H_{10}N_4O)_2]\ [Pd\ (SCN))_4]$ requires Pd, 30.22 ; SCN, 32.86%}.

### *Complex Compounds of Palladium with Guanylbutyl$^n$urea*

*Palladium*-bis-*guanylbutyl$^n$urea.*—A mixture of sodium chloropalladite (1 *M*) and guanylbutyl$^n$urea (1.5 *M*) was made alkaline with NaOH and digested on a water bath for half hour. The precipitated complex base was filtered, washed with water, dissolved in hot ethanol, and reprecipitated with water in the cold. The crystalline precipitate was collected on the filter and dried over KOH. It is slightly soluble in cold ethanol but readily so in the hot. {Found : Pd, 25.01; N, 25.86 ; $H_2O$ (by loss at 110°), 2.42. $[Pd(C_6H_{13}N_4O)_2].0.5H_2O$ requires Pd, 24.89 ; N, 26.04 ; $H_2O$, 2.09%}.

*Chloride.*—The complex base, suspended in ethanol in the cold, was neutralised with HCl (dil), resulting in a clear, pale yellow solution. This was then concentrated on a water bath to a small bulk, cooled in ice, and the complex chloride precipitated with the addition of cold water. {Found : Pd, 20.43 ; Cl, 13.23 ; $H_2O$ (at 110°), 7.04. $[Pd\ (C_6H_{14}N_4O)_2]\ Cl_2.2H_2O$ requires Pd, 20.20 ; Cl, 13.44 ; $H_2O$, 6.81%}.

*Sulphate :* {Found : Pd, 18.94 ; $H_2O$ (by loss at 110°), 6.18. $[Pd\ (C_6H_{14}N_4O)_2]\ SO_4.2H_2O$ requires Pd, 19.22 ; $H_2O$, 6.48%}. $\chi_g = -0.09\times10^{-6}$.

*Palladium*-bis-*guanylbutyl$^i$urea* was prepared as for the corresponding base of guanylbutyl$^n$urea. {Found : Pd, 25.16 ; N, 26.25. $[Pd\ (C_6H_{13}N_4O)_2]$ requires Pd, 25.34 ; N, 26.60%}.

*Palladium*-bis-*guanylamyl$^i$urea :* {Found : Pd, 23.58 ; N, 24.36. $[Pd\ (C_7H_{15}N_4O)_2]$ requires Pd, 23.76 ; N, 24.94%}. $\chi_g = -0.12\times10^{-6}$.

*Palladium*-bis-*guanylhexyl$^n$urea :* {Found : Pd , 21.82; N, 22.89 ; $H_2O$, 1.81. $[Pd\ (C_8H_{17}N_4O)_2]$-$0.5H_2O$ requires Pd, 22.04 ; N, 23.14; $H_2O$, 1.86%}.

*Equivalent Conductance*

Measurements of conductance at different dilutions were carried out at 32°. The equivalent conductance at infinite dilution was then calculated with the help of Walden's formula:

$\Lambda_\infty = \Lambda_v\ (1 + 0.6292 \times n_1 \times n_2 \times v^{-\frac{1}{2}})$, where $n_1$ and $n_2$ are the valencies of the ions.

TABLE I

A. Palladium-*bis*-guanylmethylurea chloride $[Pd\ (C_3H_6N_4O)_2]Cl_2.2H_2O$.

| Dilution (in litres) | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|
| $\Lambda v$ | 72.7 | 77.2 | 84.5 | 83.6 |
| $\Lambda_\infty$ | 81.6 | 83.9 | 89.7 | 87.2 |
| $\Lambda_{\infty\ (mean)}$ | 85.6. Mol. conduc. = 171.2. | | | |

B. Palladium *bis*-guanylethylurea chloride $[Pd(C_4H_{10}H_4O)_2]Cl_2.2.5H_2O$.

| Dilution (in litres) | 64 | 128 | 256 | 1024 |
|---|---|---|---|---|
| $\Lambda v$ | 86.3 | 95.4 | 109.0 | 118.2 |
| $\Lambda_\infty$ | 101.3 | 107.0 | 118.3 | 123.2 |
| $\Lambda_{\infty(mean)}$ | 112.4. Mol. donduc. = 224.8. | | | |

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# METAL COMPLEXES OF DI-*p*-TOLYLTHIOVIOLURIC ACID

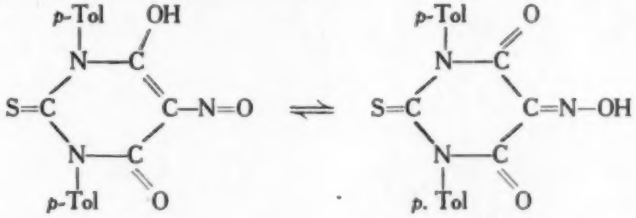
By R. P. Singh

Several metal complexes of di-*p*-tolylthiovioluric acid have been prepared. All the salts are highly coloured and appear to be metal chelates of the thiovioluric acid.

Violuric acid and its derivatives contain an oxime group, -CO-C:(NOH)-, through enolisation. This group induces the molecule of these compounds to form inner-complex salt. One of the most important reactions of compounds of this type is the so-called "iron-blue reaction", first observed by Whiteley (*J. Chem. Soc.*, 1907, **91,** 1330).

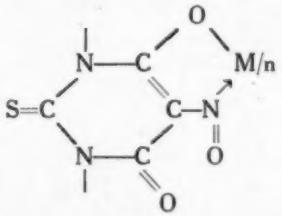
With a view to investigating analytical applications of this important class of compounds, the author prepared a number of complexes of substituted violuric acids (*Proc. Ind. Acad. Sci.*, 1946, **23A,** 330 ; *J. Sci. Ind. Res.*, 1956, **15B,** 245 ; this *Journal*, 1959, **36,** 198). The present work deals with similar complexes formed by di-*p*-tolylthiovioluric acid.

Theoretical considerations and properties of these salts suggest these to be inner complexes. The acid molecule in its nitroso-enolic form (I) contains a replaceable hydrogen atom, which can be replaced by a metal atom during salt formation.




(I) (II)

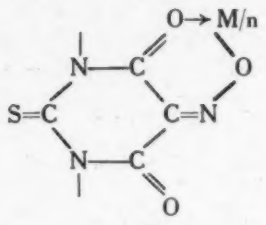
Further, the molecule contains a nitrogen atom in the 1 : 4 position with respect to the oxygen atom. By virtue of a lone pair of electrons on the nitrogen atom, it can act as a donor and form a co-ordinate link with the metal atom, effecting ring-closure. That chelation can take place readily, when the two atoms concerned in chelation are in 1 : 4 position to one another, is well known. Metallic salts of di-*p*-tolylthiovioluric acid can be represented by (III).




(III)

Alternatively, chelation can also take place through the oxygen atom of the nitroso group, which would amount to the same thing as saying that the acid reacts with the metal ions in the

oximino-ketonic form (II) and the replacement of the hydrogen atom of the oxime group would then give a six-membered ring (IV).



(IV)

It is difficult to decide between the alternative structures (III) and (IV). It is interesting to note that according to Sidgwick (*J. Chem. Soc.*, 1941, 433) the co-ordinating power of N or negative oxygen $O^-$ is roughly the same. It seems highly probable, however, that the rings in these chelates are six-membered. This would be in accordance with Pfeiffer's observations (*Angew. Chem.*, 1940, **53,** 93) that a five-membered ring is more stable when it is entirely saturated, but six-membered rings become more stable in case one or more double bonds are present.

The conclusion that the metallic derivatives of di-*p*-tolylthiovioluric acid are inner complexes is further supported by their intense colour, insolubility in water, and high solubility in non-polar solvents. The evidence of colour is usually considered as almost conclusive, and intensification of colour is usually considered as an indication of chelation. In addition to the above evidence on the basis of which chelate formation has been inferred, stable compounds of a large number of metals have been isolated in the solid state. From the results of analysis of these compounds, conclusions can be drawn concerning the arrangement of the co-ordinated groups around the central ion. We have observed that in some cases the co-ordination requirements of the metal atoms are not fulfilled in spite of chelation on account of the valency requirements of the metal atoms concerned. In view of the fact that the molecule of di-*p*-tolylthiovioluric acid contains a replaceable hydrogen atom, the number of molecules of the acid, which would react with one atom of the metal, should be equal to the valency of the metal atom concerned. The acid molecule as a whole acts as a bidentate chelate radical, and thus the co-ordination number of the metal atom will be equal to twice its valency in these compounds. This would mean that in many cases the co-ordination number of the metal atoms would be less than that expected from their behaviour in other co-ordination compounds. This type of behaviour is exhibited in several other cases, e.g., in the cobalt salt of ethyltetramethylpyrromethene-4 : 4′-dicarboxylic acid (Porter, *J. Chem. Soc.*, 1938, 368). Alternatively, it is more likely that the remaining co-ordination positions in these complexes are occupied by water molecules, or even the anions present in the solution. Basing on the results of analysis of these compounds, which would not be greatly altered by the presence or absence of water molecules or anions within the complex (because of the high molecular weights of these complexes), it is not possible at present to draw definite conclusions.

## EXPERIMENTAL

Di-*p*-tolylthiovioluric acid was synthesised by the method of Dutt *et al.* (*Proc. Ind. Acad. Sci.*, 1938, **8A,** 145). Di-*p*-tolylthiourea, obtained from *p*-toluidine and $CS_2$, was condensed with malonic acid to yield di-*p*-tolylthiobarbituric acid from which the corresponding violuric acid was obtained by the action of nitrous acid.

TABLE I

*Properties and analyses of metal complexes.*

| Salt. | Colour. | Decomp. temp. | $\lambda_{max.}$ | % Sulphur. Calc. | % Sulphur. Found | % Metal. Calc. | % Metal. Found | Metal: acid. |
|---|---|---|---|---|---|---|---|---|
| Silver | Apple green | 110° | .. | 6.96 | 6.93 | 23.45 | 23.44 | 1:1 |
| Lead | Greyish brown | 184° | 4624 Å | 7.02 | 6.98 | 22.74 | 22.71 | 1:2 |
| Mercurous | Pink | 268° | .. | 5.79 | 5.73 | 36.32 | 36.28 | 1:1 |
| Mercuric | Pale yellow | 204° | .. | 7.07 | 7.06 | 22.17 | 22.16 | 1:2 |
| Bismuth | Orange-brown | >350° | 4345 | 7.58 | 7.59 | 16.52 | 16.52 | 1:3 |
| Copper | Dark brown | 186° | 4700 | 8.33 | 8.32 | 8.28 | 8.29 | 1:2 |
| Cadmium | Pinkish orange | 255° | 4324 | 7.83 | 7.80 | 13.76 | 13.75 | 1:2 |
| Antimony(III) | Orange | 201° | 4248 | 8.15 | 8.11 | 10.33 | 10.30 | 1:3 |
| Stannous | Yellow | >350° | 4200 | 7.76 | 7.77 | 14.42 | 14.40 | 1:2 |
| Stannic | Deep orange | >350° | .. | 8.38 | 8.39 | 7.77 | 7.71 | 1:4 |
| Gold | Brownish yellow | 155° | .. | 7.66 | 7.65 | 15.74 | 15.72 | 1:3 |
| Platinum | Yellowish brown | 178° | 4800 | 7.98 | 7.98 | 12.17 | 12.19 | 1:4 |
| Cerous | Pinkish grey | 232° | 4440 | 8.02 | 8.10 | 11.71 | 11.69 | 1:3 |
| Ceric | Reddish brown | >350° | 5305 | 8.26 | 8.24 | 9.05 | 8.97 | 1:4 |
| Thorium | Grey | >350° | 4392 | 7.80 | 7.81 | 14.15 | 14.15 | 1:4 |
| Ferrous | Deep blue | 164° | 6202 | 8.42 | 8.41 | 7.35 | 7.35 | 1:2 |
| Ferric | Dark green | 172° | 6500 | 8.63 | 8.63 | 5.01 | 4.91 | 1:3 |
| Aluminium | Greyish yellow | 195° | .. | 8.86 | 9.01 | 2.49 | 2.50 | 1:3 |
| Chromium | Brownish orange | 199° | 4318 | 8.66 | 8.64 | 4.69 | 4.67 | 1:3 |
| Vanadium(III) | Orange-brown | 159° | 4732 | 8.67 | 8.65 | 4.60 | 4.58 | 1:3 |
| Vanadyl | Orange | 194° | 4850 | 8.30 | 8.31 | 6.60 | 6.62 | 1:2 |
| Beryllium | Greyish yellow | 187° | 4215 | 8.97 | 8.94 | 1.26 | 1.23 | 1:2 |
| Titanyl | Brownish orange | 193° | 4202 | 8.33 | 8.32 | 6.23 | 6.22 | 1:2 |
| Zirconium | Reddish brown | 180° | 4268 | 8.53 | 8.49 | 6.08 | 6.03 | 1:4 |
| Uranyl | Yellow | 241° | 4296 | 6.57 | 6.55 | 24.44 | 24.43 | 1:2 |
| Lanthanum | Pinkish brown | >350° | .. | 8.03 | 8.01 | 11.62 | 11.66 | 1:3 |
| Cobalt | Dark brown | 247° | 4578 | 8.38 | 8.32 | 7.72 | 7.69 | 1:2 |
| Nickel | Yellowish grey | >350° | 4752 | 8.39 | 8.36 | 7.69 | 7.65 | 1:2 |
| Manganese | Slate-coloured | 254° | 4367 | 8.43 | 8.41 | 7.23 | 7.22 | 1:2 |
| Zinc | Grey | 246° | .. | 8.32 | 8.32 | 8.49 | 8.48 | 1:2 |
| Calcium | Pink | >350° | 4356 | 8.60 | 8.61 | 5.38 | 5.37 | 1:2 |
| Strontium | Deep pink | >350° | .. | 8.08 | 7.94 | 11.06 | 11.03 | 1:2 |
| Barium | Deep pink | >350° | .. | 7.60 | 7.59 | 16.32 | 16.3 | 1:2 |
| Magnesium | Brownish orange | >350° | .. | 8.78 | 8.74 | 3.33 | 3.32 | 1:2 |
| Ammonium | Bluish grey | 164° | 5290 | 8.64 | 8.62 | .. | .. | 1:1 |
| Lithium | Orange-red | 264° | 4500 | 8.91 | 8.89 | 1.93 | 1.90 | 1:1 |
| Sodium | Light greenish | 241° | .. | 8.53 | 8.49 | .. | .. | 1:1 |
| Potassium | Green | 230° | .. | 8.18 | 8.21 | .. | .. | 1:1 |

*Metallic Salts of Di-p-tolylthioviolurie Acid.*—The ammonium salt was obtained by the addition of an excess of ammonium hydroxide to the acid, and evaporating the solution to dryness on a water bath when the ammonium salt was left behind. Alkali metal salts were similarly obtained

by dissolving the acid in minimum quantity of strong alkali solution. The solution was evaporated to dryness and the impure alkali metal salt was purified by crystallisation from water.

Salts of other metals were obtained by adding a saturated solution of the ammonium salt in water to a saturated solution of the salt of the metal concerned. The insoluble metallic salts were thrown down as precipitates. Chlorides or nitrates of metals were used in most cases.

The precipitates of the salts, thus obtained, were washed with water till free of impurities, and metal and sulphur contents were determined, the latter by oxidation to sulphate and by weighing as barium sulphate. Majority of the metals in the complexes were estimated by ignition of weighed quantities of complexes and weighing the oxides of the metals, which were left behind. In those cases, where the metal did not form an oxide of definite composition, the residue was dissolved, and the metal reprecipitated in a form suitable for its gravimetric estimation.

All the metallic salts of di-*p*-tolylthiovioluric acid are highly coloured, crystalline in nature, and are stable in the solid state as well as in organic solvents. Excepting the alkali metal salts, these are insoluble in water and soluble in organic solvents, e.g., acetone, ether and dioxan. Aqueous solutions of these salts respond to most of the tests for the corresponding cations showing that there is some dissociation in most cases. On heating the salts melt with decomposition. The silver salt is photosensitive and becomes black in about three days in diffused light. The absorption maxima of a number of these compounds were determined with the help of a constant deviation spectrograph (Hilger) and in some cases by a spectrophotometer (Unicam, S.P. 600 model). Results of analysis and some properties of the salts are recorded in Table I.

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# GUANYLALKYLUREAS AND THEIR METALLIC COMPLEXES. PART VI. COBALT(III) COMPLEXES

By R. L. Dutta, Bimanesh Sur and Nihar Ranjan Sengupta

The preparation and properties of the complex compounds of cobalt(III) with a number of guanylalkylureas comprising guanyl-$N^1$-methyl-, -ethyl-, -butyl$^n$-, -butyl$^i$-, -amyl$^i$-, and -hexyl-$^n$-ureas have been described. The complex cobalt (III)-*tris*-guanyl-$N^1$-alkylurea base and its salts are red to rose-red in colour. The conductances of some of their chloride in aqueous solution agree with the composition of tri-univalent electrolyte. All these complexes have been found to be diamagnetic and, hence, belong to the inner-level octahedral type with $d^2sp^3$ hybrid covalent bonds.

The action of KCN on the cobalt (III)-*tris*-guanyl-$N^1$-methyl- or -ethylurea base and its salts has also been studied. This has led to the isolation of dicyano-cobalt (III)-*bis*-guanyl-$N^1$-methyl- or -ethylurea base. These may be represented by [Co (R-GauH) (R-Gau) $(CN)_2$], where R=Me or Et.

The preparation and properties of copper, nickel and palladium complexes with guanylalkylureas have been described previously (this *Journal*, 1959, **36**, 567 ; 576 ; 1960, **37**,499). Rây and Bandopadhyay (*ibid.*, 1952, **29**, 865) have described the preparation and properties of the cobalt(III) complexes of unsubstituted guanylurea and $N^4$-phenylguanylurea. The cobalt(III) complexes of the guanyl-$N^1$-alkylureas have not been studied so far, and the present work records an account of the preparation and properties of the same with some of the guanyl-$N^1$-alkylureas which comprise guanyl-$N^1$-methyl-, -ethyl-, -butyl$^n$-, -butyl$^i$-, -amyl$^i$-, and -hexyl$^n$ureas. The compounds can be represented as :

I.[Co (R-GauH)$_3$] $X_3$. $nH_2O$, where R-GauH=one molecule of guanyl -$N^1$- alkylurea and X=Cl or $\frac{1}{2}SO_4$ ; R=methyl, ethyl, butyl$^n$, butyl$^i$, amyl$^i$, and hexyl$^n$ unit. These compounds are either dull red or rose-red in colour.

With the exception of cobalt(III)-*tris*-guanyl-$N^1$-hexyl$^n$urea sulphate, which is insoluble in water, the other complex cobalt(III)-guanyl-$N^1$-alkylurea sulphates are soluble in water but insoluble in ethanol and acetone.

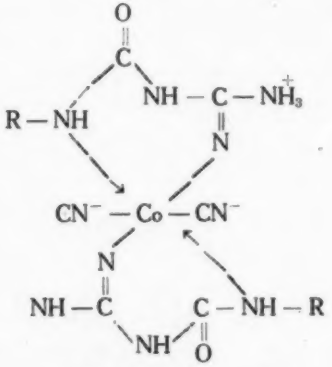
The complex cobalt(III)-guanyl-$N^1$-alkylurea chlorides are extremely soluble in water and ethanol but insoluble in acetone. The solubility of the complex chloride decreases with increase in the chain length of the substituent. A strong solution of the complex chloride has been found to give characteristic precipitates with heavier anions like dithionate, chromate, phosphate, etc. and also with many complex anions.

The conductance measurement of the complex cobalt (III)-*tris*-guanyl-$N^1$-methyl-, -ethyl-, and -butyl$^i$-urea chlorides in solution furnishes values, which agree with those for a tri-univalent electrolyte in composition. The variation of $\Delta_\infty$ values calculated from $\Delta_v$ values by Walden's formula indicates that the cobalt(III) complexes undergo partial hydrolysis in dilute solution.

II. [Co (R−Gau)$_3$]. $nH_2O$, where R=GauH = $R - NH - \underset{\underset{O}{\|}}{C} - NH - \underset{\underset{NH}{\|}}{C} - NH_2$

The solubility of these dark red complex bases in water also decreases with increase in the chain length of the substituent, whereas that in ethanol and acetone increases. The complex bases are usually hygroscopic in nature and absorb $CO_2$ from the air. They liberate ammonia from the ammonium salts and form the corresponding complex salts. On heating to 90°, the compounds lose their water and form anhydrous bases.

By treating the solution or aqueous suspension of the complex cobalt(III)-guanyl $N^1$-methyl- or -ethylurea base or their salt with potassium cyanide, either in the cold or at the temperature of the water bath, yellow complex dicyano-cobalt(III)-*bis*-guanyl-$N^1$-methyl- or -ethylurea base (anhydro-base), similar to those of the dicyano-cobalt(III)-*bis*-biguanide or substituted biguanide complexes (Sengupta and Rây, this *Journal*, 1959, **36**, 201), are formed. These can be formulated as $[Co(R\text{-}GauH)\ (R\text{-}Gau)\ (CN)_2]$; R=Me or Et. These are very sparingly soluble in water and suffer decomposition easily on boiling with water and also with acids, but are stable towards alkali solutions. The solid compounds decompose on heating to 90°. The aqueous suspension on treatment with a strong solution of ammonium salts slowly decomposes and the corresponding salts of the complex bases could not therefore be isolated in the pure state. The dicyano-cobalt (III)-*bis*-guanyl-$N^1$-methyl- and -ethylurea bases are less stable and more soluble than those of the methyl- and ethylbiguanide complexes (Sengupta and Rây, *loc. cit.*) though there is a close resemblance between them in other respects; hence the structure of the dicyano-cobalt (III)-*bis*-guanyl-$N^1$-methyl- or -ethylurea base (anhydro-base) can be represented by the following configuration:



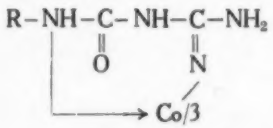
(where R = Me or Et)

The action of KCN on cobalt (III)-*tris*-guanyl-$N^1$-alkylurea (R=$Bu^n$, $Bu^i$, $Am^i$ and $hexyl^n$) results in the formation of the corresponding dicyano complexes in a rather impure state, from which the pure products could not be isolated.

The guanylalkylureas form with cobalt(II) salts in alkaline solution yellow precipitates of the complex cobalt (II)-guanyl-$N^1$-alkylureas, which oxidise to the cobalt (III) state. The complex cobalt(III)-*tris*-guanyl-$N^1$-alkylureas are all diamagnetic; hence they belong to the type of inner metallic penetration complexes with octahedral $d^2sp^3$ hybrid bonds.

Cobalt(III)-*tris*-guanyl-$N^1$-alkylurea complexes closely resemble the cobalt(III)-*tris*-biguanide and *tris*-alkylbiguanide complexes (Rây and Dutt, this *Journal*, 1939, **16**, 621; Dutta, *Z. anorg. Chem.*, 1959, **302**, 237; Sengupta, unpublished work; Ray, unpublished work) in their composition and also in their physical and chemical properties. The colour of the cobalt (III)-*tris*-guanyl-$N^1$-alkylurea complexes corresponds to those of its biguanide and alkylbiguanide complexes, except that the latter are more brightly coloured. The solubility of the two series runs in a parallel course, the biguanide complex being less soluble. The two series are more or less stable towards acids or alkalies, and have the same absorption maxima (480-485 mμ; $\epsilon_{Co\text{-}big}$ 231.5; $\epsilon_{Co\text{-}big}$-201.7). The cobalt(III)-biguanide and alkylbiguanide complexes are generally

more stable than the guanylurea and the guanylalkylurea complexes of the metal. It is also worthy of note that the cobalt(III)-guanylalkylureas are much more stable than the corresponding unsubstituted guanylurea complex, while in the biguanide series presumably the reverse holds good. The constitution of cobalt(III)-*tris*-guanyl-$N^1$-alkylurea complexes may be represented like those of the biguanide complexes with tervalent metals, as shown by Rây and Saha (this *Journal*, 1937, **14,** 670).



[Anhydro-base]

## EXPERIMENTAL

### A. *Cobalt* (III)-tris-*guanyl*-$N^1$-*methylurea*

*Sulphate.*—$CoSO_4.7H_2O$ (2.5 g.) and guanyl-$N^1$-methylurea sulphate (9 g.) (Dutta and Rây, this *Journal*, 1959, **36,** 499) were dissolved in about 30 c.c. of water and the solution was made alkaline (pH above 10) by the addition of 5*N* caustic alkali. A yellow precipitate of the cobalt (II) complex separated out, which was oxidised by adding about 10 c.c. of $H_2O_2$. Air was then passed through the resulting mixture for about half an hour when a dark red solution of the base was obtained. This was filtered and the filtrate was neutralised with $9N$-$H_2SO_4$ till the solution was just acidic to litmus. The mixture was then stirred for about 15 minutes when the rose-red complex sulphate crystallised out on cooling in ice. The crystals were filtered, washed twice with ice-cold water, then with ice-cold water-ethanol (1 : 2 by vol.), finally with ethanol, and dried in air. {Found : Co, 9.53 ; N, 27.43 ; $SO_4$, 23.22; $H_2O$ (by loss at 110°), 11.38. $[Co(CH_3.GauH)_3]_2$-$(SO_4)_3.8H_2O$ requires Co, 9.62 ; N, 27.41 ; $SO_4$, 23.49 ; $H_2O$, 11.74%}. $\chi_g = -0.045 \times 10^{-6}$.

The *complex base* was prepared by triturating in a mortar a calculated amount of the complex sulphate and baryta in 5-10 c.c. of $CO_2$-free water. The pasty mass was taken up with ethanol and filtered. The filtrate, freed of barium sulphate, was evaporated to dryness in vacuum over $CaCl_2$ and KOH. The residue was again taken up with acetone, filtered, and acetone removed by evaporation in vacuum over $CaCl_2$ and KOH, when red crystals of the complex base were obtained. {Found : Co, 11.60 ; N, 33.20 ; $H_2O$ (loss at 90°), 20.91. $[Co(CH_3Gau)_3].6H_2O$ requires Co, 11.52 ; N, 32.81 ; $H_2O$, 21.09%}.

The *complex chloride* was prepared by neutralising a solution of the complex base in acetone with HCl (dil.). The rose-red complex chloride, thus precipitated, was filtered, washed thoroughly with acetone, and finally dried over $CaCl_2$. The complex chloride is soluble in water and ethanol but insoluble in acetone. {Found : Co, 10.09 ; Cl, 17.61; $H_2O$ (by loss at 110°), 13.86. $[Co(CH_3.GauH)_3]Cl_3.4.5H_2O$ requires Co, 9.92; Cl, 17.91; $H_2O$, 13.62%}.

### B. *Cobalt* (III) tris-*guanyl*-$N^1$-*ethylurea*

The complex cobalt (III)-*tris*-gaunyl-$N^1$-ethylurea sulphate, base, and chloride were prepared in a similar manner following the procedure as described in the preparation of the guanyl-$N^1$-methylurea compounds.

*Sulphate :* {Found : Co, 8.55; N, 24.29 ; $SO_4$, 21.15 ; $H_2O$ (by loss at 110°), 13.34. $[Co(C_2H_5.GauH)_3]_2$ $(SO_4)_3.10H_2O$ requires Co, 8.64; N, 24.60; $SO_4$, 21.09; $H_2O$, 13.15%}. $\chi_g = -0.037 \times 10^{-6}$.

*Base :* {Found : Co, 13.02; N, 37.00; $H_2O$ (by loss at 90°), 2.12. [Co ($C_2H_5$ Gau)$_3$] $0.5H_2O$ requires Co, 12.97; N, 36.93; $H_2O$, 1.98%}.

*Chloride :* {Found : Co, 9.32; N, 26.22; Cl 16.76; $H_2O$ (by loss at 110°), 13.84. [Co ($C_2H_5$-GauH)$_3$]$Cl_3.5H_2O$ requires Co, 9.14; N, 26.02; Cl, 16.50; $H_2O$, 14.09%}.

C. *Cobalt* (III)-tris-*guanyl*-$N^1$-*butyl*$^n$*urea*

*Base :* (*i*). $CoSO_4.7H_2O$ (1.5 g.) in water (20 c.c.) and guanyl-$N^1$-butyl$^n$urea sulphate (6g.) in 50 c.c. of water were mixed together and to the mixture 5*N* alkali was added dropwise till it was strongly alkaline. To this mixture containing a yellow precipitate of cobalt (II) complex 10-15 c.c. of $H_2O_2$ was added with constant stirring. The resulting mixture was warmed on a water bath for about half an hour when a dark red oil collected at the bottom. The mother liquor was decanted and the oil was washed with water. Finally, the oil was treated with ice-cold water and stirred thoroughly when it began to solidify. This was filtered, washed with water, and then recrystallised from acetone. The red compound was dried over $CaCl_2$ and KOH.

(*ii*). The same compound was also obtained in a pure state by the interaction of cobalt (III) hexammine chloride and alkaline guanyl-$N^1$-butyl$^n$urea sulphate at the temperature of water bath, when a dark red oil separated, from which the pure compound was obtained as described in the previous method. {Found : Co, 11.26; N, 31.03. [Co ($C_4H_9$Gau)$_3$] requires Co, 11.14; N, 31.07%}.

The *complex sulphate* was obtained by neutralising the ethanolic solution of the complex base with $H_2SO_4$ (dil.). The product was filtered, washed with ethanol, and dried in air. It is fairly soluble in water but insoluble in ethanol and acetone. {Found : Co, 8.63; N, 24.04; $SO_4$, 20.90; $H_2O$ (by loss at 100°), 3.87. [Co ($C_4H_9$. GauH)$_3$]$_2$ ($SO_4$)$_3$.$3H_2O$ requires Co, 8.38; N, 23.86; $SO_4$, 20.45; $H_2O$, 3.83%}. $\chi_g = -0.069\times10^{-6}$.

In a similar manner the cobalt (III)-*tris*-guanyl-$N^1$ -butyl$^i$-, -amyl$^i$- and -hexyl$^n$urea complexes were prepared and their properties studied.

D. *Cobalt* (III)-tris-*guanyl*-$N^1$ -*butyl*$^i$*urea*

*Base :* {Found : Co, 10.91; N, 30.31; $H_2O$ (by loss at 90°), 3.01. [Co ($C_4H_9$. Gau)$_3$]$H_2O$ requires Co, 10.75; N, 30.65; $H_2O$, 3.28%}.

*Sulphate :* {Found : Co, 7.43 ; N, 24.01; $SO_4$, 18.31; $H_2O$ (by loss at 100°), 14.75. [Co ($C_4H_9$. GauH)$_3$]$_2$ ($SO_4$)$_3$, $13.5H_2O$ requires Co, 7.39; N, 24.07; $SO_4$, 18.04; $H_2O$, 14.84%}. $\chi_g = -0.059\times10^{-6}$.

The *chloride* was prepared by neutralising the acetone solution of the complex base with HCl (dil.). {Found : Co, 8.92; N, 25.62; Cl, 15.79; $H_2O$ (by loss at 110°), 4.32. [Co ($C_4H_9$ GauH)$_3$]$Cl_3$ requires Co, 8.87; N, 25.24; Cl, 16.01; $H_2O$, 4.06%}.

E. *Cobalt* (III)-tris-*guanyl*-$N^1$-*amyl*$^i$*urea*

*Base :* {Found : Co, 9.95; N, 28.56; $H_2O$ (by loss at 90°) 1.71. [Co ($C_5H_{11}$ Gau)$_3$] $0.5H_2O$ requires Co, 10.16; N,28.91; $H_2O$, 1.55%}.

F. *Cobalt* (III)-tris-*guanyl* $N^1$-*hexyl*$^n$*urea*

*Base :* {Found : Co, 8.86; N, 26.01; $H_2O$ (by loss at 90°), 5.74. [Co ($C_6H_{13}$ Gau)$_3$] $2H_2O$ requires Co, 9.07; N, 25.84; $H_2O$, 5.54%}.

*Sulphate :* {Found : Co, 6.97; N, 19.10; $SO_4$, 16.37. [Co $(C_6H_{13}\ GauH)_3]_2(SO_4)_3$. $12H_2O$ requires Co, 6,81; N, 19.40; $SO_4$, 16.62%}. The complex sulphate decomposes on heating to 80°.

TABLE I

*Conductance of cobalt* (III)-tris-*guanylalkylurea chloride.*

Temp. = 35° ± 1°.

| $v$ (litres) | *N*/32 | *N*/64 | *N*/128 | *N*/256 | *N*/512 | *N*/1024 | |
|---|---|---|---|---|---|---|---|
| $\Delta_v$(methyl) | 93.07 | 90.18 | 101.12 | 110.8 | 125.7 | 139.6 | $\Delta_\infty$=128.6. Molar conductivity=385.8 |
| $\Delta_\infty$ | 127.2 | 113.6 | 119.8 | 124.9 | 137.3 | 148.7 | |
| $\Delta_v$(ethyl) | .. | .. | 81.30 | 95.41 | 107.0 | 130.5 | $\Delta_\infty$=114.9. Molar conductivity=344.7 |
| $\Delta_\infty$ | .. | .. | 96.36 | 107.8 | 116.8 | 138.8 | |
| $\Delta_v$(butyl?) | .. | 86.28 | 104.7 | 116.3 | 125.7 | 141.5 | $\Delta_\infty$=130.4. Molar conductivity=391.2 |
| $\Delta_\infty$ | .. | 108.7 | 123.0 | 131.4 | 137.2 | 150.7 | |

$\Delta_\infty = \Delta_v\ (1 + 0.692 \times n_1\ n_2.\ v^{-\frac{1}{2}})$ (Walden's formula), where $n_1$ and $n_2$ are the valencies of the cations and anions respectively, and '$v$' indicates dilution in litres.

*Dicyano-cobalt* (III)-bis-*guanyl*-$N^1$-*methyl- and-ethylurea Complexes*

To a concentrated solution of cobalt (III)-*tris*-guanyl-$N^1$-methyl (and ethyl) urea base or its salts a strong solution of KCN was added, and the resulting solution was warmed on a water bath for a short period till the orange-red solution assumed a golden yellow colour. This was then kept in a desiccator containing $CaCl_2$ and KOH, where yellow crystals of the dicyano complex separated slowly. In the case of guanyl-$N^1$-ethylurea complex the crystals appeared after a long time (5-7 days) and the yield was very poor. The products were filtered, washed first thoroughly with water, then with ethanol, and finally dried over $CaCl_2$ and KOH.

*Dicyano-cobalt* (III)-bis-*guanyl*-$N^1$-*methylurea* (anhydro-base) : {Found : Co, 17.42; N (total), 41.02. [Co $(CH_3.C_2N_4H_5).\ (CH_3.C_2N_4H_4).\ (CN)_2$] requires Co, 17.36; N, 41.18%}.

*Dicyano-cobalt* (III)-bis-*guanyl*-$N^1$-*ethylurea* (anhydro-base) : {Found : Co, 16.12; N (total), 37.45. [Co $(C_2H_5.C_2N_4H_5)\ (C_2H_5C_2N_4H_4).\ (CN)_2$] requires Co, 15.95; N, 37.84%}.

*Methods of Analysis*

Cobalt in the complex was estimated as $CoSO_4$ after ignition with strong $H_2SO_4$. Nitrogen was estimated as usual by Kjeldahl's method, and the anions by the usual standard procedure.

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# METAL CHELATES OF αβ- DIOXIMINOACETOACETAMIDES*

BY J. S. DAVE AND A. M. TALATI

The dioximes, prepared from acetoacet(aryl) amides (where aryl amide may be anilide, *o*-toluidide, *o*-chloranilide, *p*-phenetidide or 2:4-xylidide), have been used for the preparation of copper, nickel, cobalt, and palladium chelates. The magnetic susceptibilities of some of these chelates have been determined, and their structures suggested.

The metal chelates of α-dioximes have been studied by several workers (Tschugaeff, *Z. anorg. Chem.*, 1905, **46,** 144 ; *J. prakt. Chem.*, 1907, *ii*, **75,** 157 ; Pfeiffer *et al.*, *Ber.*, 1928, **61,** 103 ; 1930, **63,** 1811 ; Sugden, *J. Chem. Soc.*, 1932, 246 ; 1935, 621 ; Dwyer and Mellor, *J. Amer. Chem. Soc.*, 1935, **57,** 605 ; Banks and Haar, *ibid.*, 1955, **77,** 324). In the present investigation, the formation of metal chelates by the dioximes derived from acetoacet(aryl)amides (where aryl amide may be anilide, *o*-toluidide, *o*-chloroanilide, *p*-phenetidide or 2 : 4-xylidide) with copper, nickel, cobalt, and palladium has been studied and the magnetic susceptibilities of some of the metal chelates formed have been determined. It has been observed that these dioximes form brown paramagnetic chelates with copper, yellow, orange or red diamagnetic chelates with nickel, chocolate brown paramagnetic chelates with cobalt, and yellow or red diamagnetic chelates with palladium. Copper, nickel, and palladium chelates are formulated as $M(DH)_2$, where M = Cu, Ni or Pd and $DH_2$ is a dioxime molecule, and cobalt chelates as $Co(DH)_2.2H_2O$.

## EXPERIMENTAL

The dioximes were prepared from the corresponding acetoacet(aryl)amides as mentioned earlier (*Curr. Sci.*, 1957, **26,** 326). *αβ-Dioximinoacetoacet-p-phenetidide* : m.p. 202-203°. (Found : N, 16.10. $C_{12}H_{15}O_4N_3$ requires N, 15.84%). *αβ-Dioximinoacetoacet-2 : 4-xylidide* : m.p. 194-95°. (Found : N, 17.0. $C_{12}H_{15}O_3N_3$ requires N, 16.86%).

### *Copper, Nickel and Palladium Chelates*

The metal chelates were precipitated under specific conditions as mentioned below. These precipitates were digested on a water bath for about an hour, filtered, washed with water and ethanol, and dried at 110-20°.

(*a*). Copper chelates were obtained as brown precipitates on adding an ethanolic solution of the dioxime (0.011 *M*) to a warm, slightly acidified solution of copper chloride (0.005 *M*).

(*b*). Nickel chelates were obtained as yellow, orange or red precipitates on adding an ethanolic solution of the dioxime (0.011 *M*) to a warm, neutral solution of nickel chloride (0.005 *M*).

(*c*). Palladium chelates were precipitated as yellow or red precipitates on adding an ethanolic solution of the dioxime (0.0055 *M*) to a warm, fairly acidified solution of palladium chloride (0.0025 *M*).

### *Cobalt Chelates*

Cobalt chelates were prepared by mixing an acidified solution of the cobalt chloride (0.005 *M*) with the ethanolic solution of the dioxime (0.011 *M*). On adding ammonium acetate to the mixed clear solution, chocolate brown precipitates appeared. The reacting solution was kept at room temperature for about an hour. The precipitates were filtered, washed with water and ethanol, and air-dried. The dried precipitates did not lose water on heating to 110-20°. The metal chelates, thus obtained, together with their colour, m.p. and analysis (micro) are recorded in Table I.

* Presented at the Symposium of Co-ordination Chemistry, Agra, Feb. 7, 1959.

TABLE I

*Magnetic susceptibilities.*

| No. | Substance. $M(C_4H_5N_3O_3R)_2$: M. | R. | Colour. | M. P. | %Metal (micro). Found. | Calc. |
|---|---|---|---|---|---|---|
| 1. | Ni | phenyl | Orange-yellow | > 280° | 11.61 | 11.76 |
| 2. | Ni | o-tolyl | Orange | ,, | 11.13 | 11.13 |
| 3. | Ni | o-chlorophenyl | Orange-red | ,, | 10.45 | 10.33 |
| 4. | Ni | p-ethoxyphenyl | Deep red | ,, | 10.23 | 9.99 |
| 5. | Ni | 2:4-xylyl | Orange-red | ,, | 10.20 | 10.57 |
| 6. | Cu | phenyl | Brown | 235° | 13.06 | 12.61 |
| 7. | Cu | o-tolyl | ,, | 250° | 11.92 | 11.94 |
| 8. | Cu | o-chlorophenyl | ,, | 232° | 11.34 | 11.09 |
| 9. | Cu | p-ethoxyphenyl | ,, | 221° | 10.47 | 10.73 |
| 10. | Cu | 2:4-xylyl | ,, | 242° | 11.86 | 11.34 |
| 11. | Pd | phenyl | Yellow | > 280° | 19.55 | 19.50 |
| 12. | Pd | o-tolyl | ,, | ,, | 18.40 | 18.55 |
| 13. | Pd | p-ethoxyphenyl | ,, | ,, | 17.01 | 16.80 |
| 14. | Pd | 2:4-xylyl | Orange-red | ,, | 18.23 | 17.69 |
| | $Co(C_4H_5N_3O_3R)_2.2H_2O$: | | | | | |
| 15. | Co | phenyl | Chocolate-brown | ,, | 11.29 | 11.01 |
| 16. | Co | o-chlorphenyl | ,, | ,, | 9.87 | 9.76 |
| 17. | Co | p-ethoxyphenyl | ,, | ,, | 9.38 | 9.55 |
| 18. | Co | 2:4-xylyl | ,, | ,, | 10.26 | 9.96 |

Magnetic susceptibilities of some of these chelates were determined using Gouy's magnetic balance. The field strength used was about $5\times10^3$ gauss. The results are recorded in Table II.

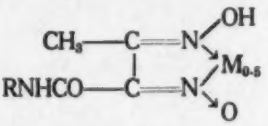
TABLE II

| *Substance No. | $X_g\times10^6$. | $X_M\times10^6$. | $X_M\times10^6$. | T (Abs.). | $\mu_{eff}$ (B.M.). |
|---|---|---|---|---|---|
| 1 | −0.270 | −134.7 | .. | 304.0 | Diamag. |
| 2 | −0.285 | −150.2 | .. | 308.0 | ,, |
| 5 | −0.308 | −171.0 | .. | 304.5 | ,, |
| 6 | +2.32 | +1169 | +1365 | 304.5 | +1.83 |
| 7 | +2.30 | +1224 | +1444 | 307.0 | +1.89 |
| 11 | −0.553 | −302.5 | .. | 305.0 | Diamag. |
| 13 | −0.609 | −386.7 | .. | 308.0 | ,, |
| 15 | +2.34 | +1211 | +1408 | 304.1 | +1.85 |
| 18 | +2.10 | +1207 | +1451 | 308.0 | +1.90 |

* The number corresponds to those in Table I.

## DISCUSSION

Nickel and palladium chelates with the dioximes are formulated as :

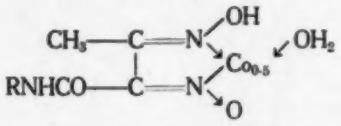


where M = Ni or Pd and R = $C_6H_5$-, *o*-$CH_3C_6H_4$-, *o*-$ClC_6H_4$-, *p*-$C_2H_5OC_6H_4$ -or 2 : 4-$(CH_3)_2C_6H_3$.

Nickel and palladium chelates are diamagnetic, and hence are considered to have a square planar configuration involving $dsp^2$ bonds. Although *cis* and *trans* isomers of these chelates can exist, only one product is obtained in each case, and is considered to have a *trans* structure (Brady and Muers, *J. Chem. Soc.*, 1930, 1599 ; Voter *et al.*, *Anal. Chem.*, 1951, **23**, 1730).

Copper chelates have a structure similar to those of nickel and palladium and have the magnetic moment of 1.8-1.9 B.M. Of the two possible square planar structures : $3d4s4p^2$ and $4s4p^24d$ for the copper chelates, the first structure involves raising of the unpaired electron to the higher energy level and its magnetic moment will be very near to that calculated by the spin-only formula because of the quenching of the orbital moment by the crystal field. On the other hand, the second structure will have a considerably higher value of the magnetic moment as the electron in the inner shell is considerably shielded from the quenching effect of the external field. Hence the copper chelates under investigation are considered to have $3d4s4p^2$ square planar structure and to represent *trans* structure (Rây and Sen, this *Journal*, 1948, **25**, 473).

Cobalt chelates with the dioximes may be formulated as :



with 6-covalent octahedral structure or as in the case of nickel, copper and palladium having a 4-covalent square planar structure with two water molecules outside the complex. It has been shown by Figgis and Nyholm (*J. Chem. Soc.*, 1954, 12) that a 4-covalent square planar cobalt(II) complex with $dsp^2$ bonds gives a moment value of 2.1-2.9 B.M., while its 6-covalent octahedral complex with $d^2sp^3$ bonds gives a somewhat lower moment value of 1.73-2.00 B.M. (cf. also Rây and Sen, *loc. cit.*). The measured moment values (1.85-1.90 B.M.) for the cobalt chelates described in this paper agree with that for the sexicovalent octahedral structure. This is also confirmed by the fact that the cobalt chelates do not lose their water molecules even at 120°.

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# SPECTROSCOPIC STUDIES ON THE OXIDATION PRODUCTS OF SUBSTITUTED THIOCARBAMIDES

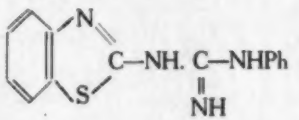
By K. S. Suresh and C. N. R. Rao

The infrared and the near ultraviolet spectra of the oxidation products of *N*-substituted aromatic thiocarbamides have been studied. Tentatively 2-guanidobenzothiazole, 3-formamidobenzothiazole and 1:2:4-thiadiazole structures have been assigned to the various products.

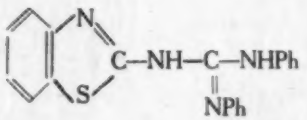
The oxidation of aromatic thiocarbamides leads to the formation of heterocyclic bases : benzothiazoles or "thiodiazoles" (this *Journal*, 1960, **37**, 25 ; *B.H.U.J. Sci. Res.*, 1958-59, **9**,94), depending on the conditions of reaction. Of these the "thiodiazoles" have been assigned a 1 : 2 : 4 structure (Hofmann and Gabriel, *Ber.*, 1892, **25**, 1578 ; Hector, *Ber.*, 1892, **25**, 799), but no definite evidence has been put forward to support this point of view. A detailed chemical investigation of the Hugershoff's base, obtained by the oxidation of *NN'*-diphenylthiocarbamide, has been already reported (*loc. cit.*, 1960), and the chemistry of Hector's base, the oxidation product of phenylthiocarbamide, has also been discussed (*loc. cit.*, p. 94). With a view to obtaining further information on their structures, a spectroscopic investigation of these and related compounds has been undertaken. In this connection we have also investigated in detail the infrared and the near ultraviolet spectra of a number of related derivatives of guanidine and benzothiazole (Suresh *et al.*, *J. Sci. Ind. Res.*, 1960).

The systems now studied are the following, of which compounds (I) to (VII) are of known constitution and (VIII), (IX) and (X) are of yet undecided structures.

(*i*). Products obtained by heating *N*-(2-benzothiazolyl)-*N'*-phenylthiocarbamide with ammonia (I), $C_{14}H_{12}N_4S$ (*loc. cit.* p. 94), and aniline (II), $C_{20}H_{16}N_4S$ (Suresh and Joshua, *Proc. Ind. Sci. Cong.*, 1960, Part III, p. 152) in presence of lead oxide, where the products should have the structures (A) and (B).

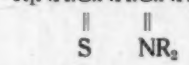



(A)




(B)

(*ii*). Products obtained by oxidation of formamidothioureas (also called guanylthioureas) of the following structure :




(C)

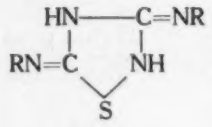
(III), $C_3H_6N_4S$, obtained by the oxidation of (C) (where $R_1$=Me ; $R_2$=$R_3$=H) which is prepared by the condensation of methyl *iso*thiocyanate and guanidine carbonate. The structure of this thiourea is unequivocal, and by oxidation can lead to a triazole or a thiadiazole of which the latter structure is almost certain (Kurzer, *J. Chem. Soc.*, 1955, 2288).

(IV), $C_8H_8N_4S$, obtained by the oxidation of (C) (where $R_1$ = Ph ; $R_2$ = $R_3$ = H) (Kurzer, *J. Chem. Soc.*, 1956, 2345).

(V), $C_{14}H_{12}N_4S$, obtained by the oxidation of (C) (where $R_1$=$R_3$=Ph ; $R_2$=H) (Kurzer, *ibid.*, 1956, 2345 ; Suresh, *loc. cit.*, p. 94).

(VI), $C_{20}H_{16}N_4S$, obtained by the oxidation of (C) (where $R_1=R_2=R_3=Ph$) (Suresh and Joshua, *loc. cit.*).

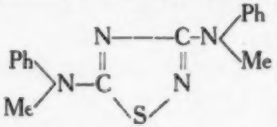
The oxidation products (III), (IV), (V), (VI) definitely possess the 1 : 2 : 4-thiadiazole structure (D)



(D)

because the formamidothioureas, from which these are formed, are obtained by the condensation of mustard oil and the corresponding guanidine as well as by the action of appropriate amine on the aryl thiuret (Dixit, under publication). The oxidation products cannot be isomeric benzothiazoles because the benzothiazole derivatives corresponding to (V) and (VI) are represented by (I) and (II), and the derivative corresponding to (IV) has also been described (Smith *et al.*, *J. Amer. Chem. Soc.*, 1931, **53,** 4103). There is no such possibility corresponding to (III).

(*iii*). Hofmann and Gabriel's thiadiazole (VII), $C_{16}H_{16}N_4S$, obtained by the oxidation of *N*-methyl-*N*-phenylthiocarbamide (*loc. cit.*). This must be represented by structure (E). An isomeric benzothiazole structure is not possible in this case (*loc. cit.*, 1960).



(E)

(*iv*). Hugershoff's base (VIII), $C_{26}H_{20}N_4S$, formed by the oxidation of *NN'*-diphenylthiocarbamide, cannot be represented by a 1 : 2 : 4-thiadiazole structure and may have the structure (G) or (H) (*vide infra*).

(*v*). Hector's base (IX), $C_{14}H_{12}N_4S$, the oxidation product of phenylthiocarbamide of yet undecided structure (*loc. cit.*, p. 94).

(*vi*). Product (X), $C_{20}H_{16}N_4S$, obtained by the bromine oxidation of an equimolar mixture of phenylthiocarbamide and *NN'*-diphenylthiocarbamide in an ethanolic medium (Sahasrabudhey and Suresh, *Proc. Ind. Sci. Cong.*, 1959, Part III, p. 135), also of undecided structure.

## EXPERIMENTAL

All the compounds were prepared in this laboratory and subjected to necessary purification, analysis and identification before taking the spectra. The infrared spectra were recorded using a Perkin-Elmer recording spectrophotometer, Model-21, and Baird-Atomic spectrophotometer, both with NaCl optics. The samples were prepared as mulls in nujol in the case of solids. Some compounds were run in chloroform solution in liquid cells. The relevant frequencies are tabulated in $cm^{-1}$ and the relative intensities of the bands recorded as follows : s, strong ; m, medium ; w, weak, and b, broad. The ultraviolet absorption spectra were recorded employing a Cary recording spectrophotometer or a Beckman DU spectrophotometer. The wave lengths are given in Å and the intensities in terms of log $\epsilon$ at the absorption maxima.

The ultraviolet spectra of all the compounds are summarised in Table I and the major frequencies in the infrared spectra of (I), (II), (VIII), (IX) and (X) in Table II and (III) to (VII) in Table III.

## TABLE I

*Near UV absorption spectra of* (I *to* X).

| Compounds. | In 47% ethanol. | | | Log ε | In 0.1*N*-NaOH. | | | In 0.1*N*-$HClO_4$. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 2230(2) | 2430* | 3115(1) | 4.45(1) | 2230(2) | 2430* | 3120(1) | 2230(1) | 2420* | 2970(4) |
| | | 2500* | | | | 2500* | | | 2730(2) | |
| | | 2840* | | | | 2830* | | | 2870(3) | |
| | | 2930* | | | | 2930* | | | | |
| II | 2220(2) | 2570(4) | 3200(1) | 4.29(1) | 2560* | 2850* | 3250(1) | 2580 | 2820* | 3200 |
| | | 2845(3) | | | | 2970** | | | 3000** | |
| | | 2970* | | | | | | | | |
| III† | 2580 | | | 4.39 | | | | | | |
| IV† | 2430(2) | 2870(1) | | 4.16(1) | | | | | | |
| | | | | 4.06(2) | | | | | | |
| V† | 2700 | 3000** | | 4.31 | | | | | | |
| VI† | 2740 | 3150* | | 4.40 | | | | | | |
| VII† | 2420* | 2650 | | 4.37 | | | | | | |
| VIII | 2850 | 3000* | | 4.48 | 2850** | 3000 | | 2700 | 3000* | |
| IX | 2360 | 2600* | | 4.26 | 2360 | 2600* | | 2500 | 2800*** | |
| X | 2520 | 2920* | | 4.46 | 2520 | 2910* | | 2540 | 2900** | |

N.B. (a) *Shoulder **Weak shoulder ***Very weak shoulder

(b) The numbers in parentheses refer to the relative intensities of the absorption maxima.
(1) refers to the most intense absorption maximum
†In absolute ethanol.

## TABLE II

*Infrared spectra of* I, II, V, VIII, IX *and* X.

| (I). | (II). | (V). | (VIII). | (IX). | (X). |
|---|---|---|---|---|---|
| 3415 mw | 3367 mw | 3378 m | 3300 mw | 3300 mw | 3350 mw |
| 1608 s | 1603 s | 3184 m | 1650 s | 1620 s | 1638 s |
| 1587 m | 1587 m | 1608 s | 1595 s | 1588 s | 1580 s |
| 1564 s | 1574 s | 1582 s | | | |
| | 1536 s | 1543 s | 1550 m | 1538 s | 1540 ms |
| 1492 s | 1471 s | 1504 m | 1500 s | 1485 m | 1525 m |
| 1440* | 1435 s | | | 1470 sh | 1490 m |
| 1350* | 1351 ms | | 1330 s | 1320 m | 1347 s |
| 1309 w | 1300 m | | 1320 s | 1300 w | 1310 ms |
| 1280 mw | 1279 s | | 1287 w | 1276 mw | 1277 w |
| 1245 m, 1210 s | 1239 ms | 1248 m, 1215 w | 1225 m | 1244 s | 1255 w, 1240 w |
| 1152 mw | 1189 m, 1149 m | 1183 w | 1160 w, 1180 w | 1163 w | 1170 mw |
| 1114 mw | 1117 w | 1159 w | | | |
| | | | | 1108 s | |
| 1060 mw | 1071 w | 1086 w | 1080 w | 1060 w | 1070 mw |
| 1020 mw | 1025 m | 1031 w | 1030 w | 1035 m | 1030 s |
| 1010 w | 1010 w | | | | |
| 970 bs | 975 s | | | | |
| 942 m | 920 s | | 915 w | 919 w | 920 w |
| 932 m | 905 m | | 900 m | 900 m | 900 m |
| | | | 890 w | 886 ms | 890 m |
| 850 w | 847 mw | 859 w | | 847 ms | 870 m |
| 795 ms | 788 mw | | 798 m | 800 m | 790 s |
| 727 s | 723 ms | 736 s | 733 s | 743 s | 725 b |
| 705 mw | 710 ms | | 715 b | 720 ms | 703 s |

*Shoulder

TABLE III

*Infrared spectra of 1:2:4-thiadiazole derivatives.*

| (III). | (IV). | (V). | (VI). | (VII). |
|---|---|---|---|---|
| 3278 s | 3412 ms | 3378 m | 3144 m | .. |
| 3154 s | 3257 ms<br>3154 s | 3184 m | .. | .. |
| 1666 s | 1652 s<br>1628 s<br>1605 s | 1608 s | 1639 s<br>1605 s | 1600* |
| 1572 s | 1570 s | 1582 s | 1558 s | 1587 m |
| 1534 s | 1529 s | 1543 s | .. | 1548 s |
| 1499 s | 1504 s | 1504 m | 1499 bs | 1488 s |
| 1224 s | 1222 s | 1248 m<br>1215 w | 1239 w | 1271 ms |
| 1170 ms | 1179 m | 1183 w | 1174 * | 1170 ms |
| 1117 ms | 1101 w<br>1080 w | 1159 w<br>1086 w | 1073 w | 1116 m<br>1076 w |
| 1050 w | 1043 ms | .. | 1054 w | .. |
| 1022 m | 1031 ms | 1031 w | 1021 w | 1028 w |
| 828 s | 836 s | 859 w | 856 w<br>795 m | 833 w<br>812 w |
| 738 s | 742 s | 736 s | 742 m | 727 ms |

* Shoulder

## DISCUSSION

The near ultraviolet spectra of (I) and (II) in ethanol solutions are very similar to those of simple 2-substituted benzothiazole derivatives (Suresh *et al.*, *loc. cit.*). For comparison, the spectra of (I) and (II) are reproduced in Fig. 1 with the spectrum of 2-anilinobenzothiazole. (II) shows some of the absorption maxima at longer wave lengths than (I). This is probably because of the greater number of phenyl groups in the former compound. Such bathochromic shifts, caused by the increase in the number of phenyl groups, are due to the increased resonance interaction (Robertson and Matson, *J. Amer. Chem. Soc.*, 1950, **72,** 5250). Both (I) and (II) show the expected variation in their ultraviolet spectra in acid solution (hypsochromic shifts) (Table I, column 3) due to protonation of imido or/and amino groups.

The infrared spectrum of (I) shows only one N—H stretching absorption around 3400 $cm^{-1}$, which is in agreement with structure (A). Both (I) and (II) exhibit a strong band around 1650 $cm^{-1}$ probably due to the >C=N vibration interacting with the aromatic vibrations. Simple guanidines also exhibit the >C=N vibration around 1600 $cm^{-1}$ (Suresh *et al.*, *loc. cit.*). Further, (I) and (II) exhibit bands in the region characteristic of the benzothiazole nucleus (*loc. cit.*). In addition these show characteristic guanidine vibrations (*loc. cit.*). The infrared spectra completely support the earlier suggestion that the guanidine units are attached in the 2-position to the benzothiazole nucleus in (I) and (II).

FIG. 1

*UV absorption spectra of 2-guanidinobenzothiazoles* (I *and* II) *and 2-anilinobenzothiazole.*

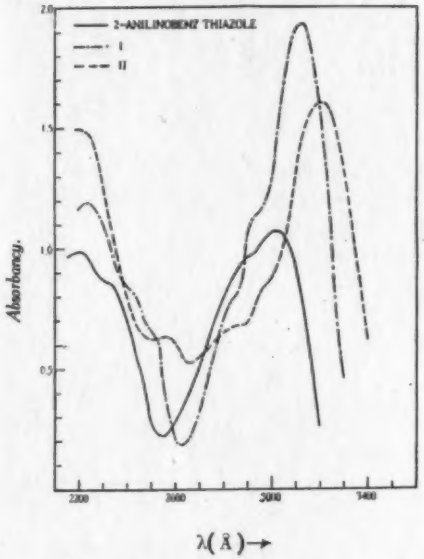
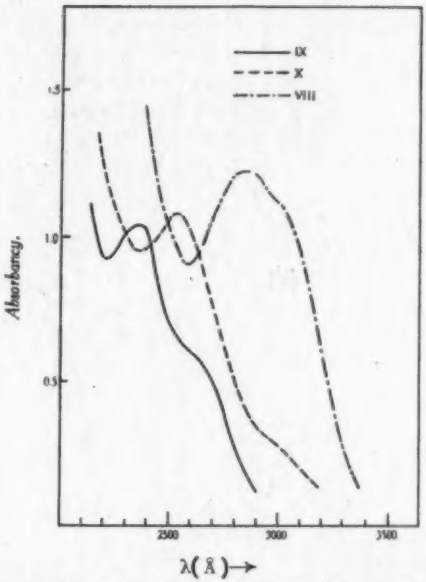


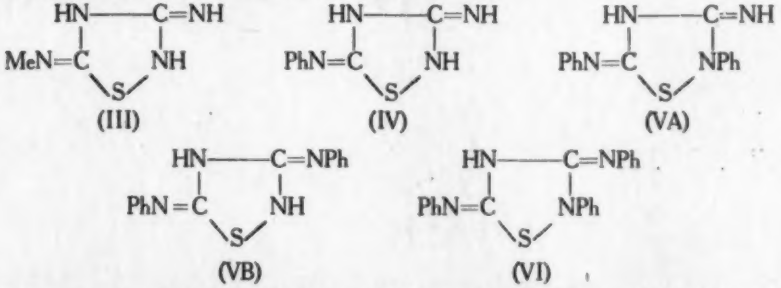

FIG. 2

*UV absorption spectra of the oxidation products of aromatic thiocarbamides* (VIII, IX *and* X).




The UV spectra of (III) to (VII) are also summarised in Table I. The bathochromic shifts going from (IV) to (VI) are not uniformly increasing because the aromatic character or the extent of conjugation itself will be different in these systems, as shown by the structures mentioned below for these compounds. The intensity of the band increases, however, with the number of phenyl groups. The spectra of these thiadiazoles are in a way similar to the spectra of the thiadiazoles reported by Goerdeler *et al.* (*Chem. Ber.*, 1954, **87**, 61).

The frequencies that consistently appear in the infrared spectra of thiadiazoles are summarised in Table III. The infrared data on these compounds (III through VI) can be interpreted on the basis of the thiadiazole structures for these compounds.



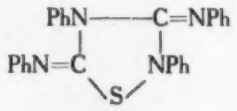

All these compounds show bands due to N—H stretching in the region 3150-3400 $cm^{-1}$. The number of N—H stretching bands depends on the types of N—H linkages. In cases like (III), (IV) and (V), there are imine and secondary amine type of N—H linkages. However, in (VI) only

secondary amine N—H type is possible, and rightly so only one band is observed. It is understood that the frequencies observed are rather lower than that expected due to hydrogen bonding in solid state. Because of the two N—H stretching bands observed in (V), the structure (VB) is more likely (*loc. cit.*, 1960). This evidence is, however, not conclusive enough. All these derivatives (III to VI) show bands in the region 1570-1670 $cm^{-1}$, possibly due to C=N linkages. An exclusive assignment is not possible since most of them have C = C due to phenyl groups. But in (III), which has only a methyl group as a substituent, the bands at 1572 $cm^{-1}$ and 1666 $cm^{-1}$ cannot be due to phenyl groups, but are probably due to the C = N linkages. All the compounds (III to VI) show a number of bands consistently in the finger print region. Of course, compounds with a greater number of phenyl groups show a greater number of extra weak or medium intensity bands in this region. From a survey of the frequencies tabulated in Table III, it is seen that at least a few of the frequencies in the region 710-1100 $cm^{-1}$ may be characteristic of the thiadiazole heterocycle. Other characteristic frequencies due to phenyl groups, etc. are also seen, but not tabulated. On the whole, the infrared spectra of (III) to (VI) show an overall similarity.

Compound (VII), obtained by the oxidation of *N*-methyl-*N*-phenylthiocarbamide, exhibits the infrared spectrum very similar to the 1 : 2 : 4-thiadiazoles (III to VI). The major frequencies of (VII) are shown in Table III. It is interesting to see that (VII) does not show any N—H stretching vibration as is to be expected if the structure were (E) (*vide supra*).

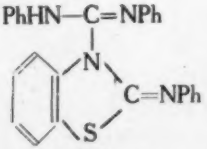
The ultraviolet spectra of (VIII), (IX), and (X) are markedly different from those of simple benzothiazole derivatives (Fig. 1). All the three derivatives show an absorption maximum and a shoulder at a longer wave length. They exhibit progressively increasing bathochromic shifts in the order: (IX), (X) and (VIII) (the number of phenyl groups increasing in the same order). The spectra of (IX), (X), and (VIII) in ethanol are reproduced in Fig. 2. The intensities of the bands also increase with the number of phenyl groups. The variations of the UV spectra in acid solution are not straightforward in these derivatives (Table I). The results of UV spectra only indicate that (IX), (X), and (VIII) may be very similar. The UV spectra resemble those of 2-imino-2 :3-dihydrobenzothiazole derivatives (Edisbury *et al.*, *J. Chem. Soc.*, 1948, 1497) and also some of the 1 : 2 : 4-thiadiazole (Goerdeler, *loc. cit.*).

The infrared spectra of these derivatives also show a great similarity to one another. Compound (VIII) (which should have four phenyl groups according to elemental analysis) shows a N—H stretching frequency at 3300 $cm^{-1}$ (even in a solution spectrum). Chemical evidence also indicates an active hydrogen (this *Journal*, 1960, *loc. cit.*). This excludes the 1: 2: 4-thiadiazole structure (F) for this compound :

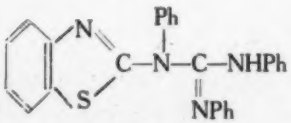



(F)

So (VIII) may be a more complex derivative of benzothiazole (assuming that this is the only other possibility—chemical evidence apparently indicates the presence of a benzothiazole nucleus) of the type (G) or (H).




(G)




(H)

A simple structure of the type (H) is, however, difficult to support on the basis of the UV spectrum. Further, (VIII), (IX) and (X) do not show characteristic vibrations of benzothiazole and guanidine as well, as shown by (I) and (II). It is known that the 2 : 3-dihydrobenzothiazole system shows deviations in the infrared spectra from the simple 2-substituted benzothiazoles (Suresh *et al.*, *loc. cit.*). These observations can be explained by the structure (G) for (VIII). The C=N frequencies interacting with C=C of the phenyl groups in (IX), (X) and (VIII) are seen at 1620, 1638 and 1650 $cm^{-1}$ respectively, showing progressive increase in the frequency with the number of phenyl groups. The frequency variations are possibly due to the bond-order changes caused by the presence of phenyl groups. Also, the complexity of the spectra of (IX), (X), and (VIII) increases in the skeletal region with increase in the number of phenyl groups. The infrared spectrium of (IX) shows some similarity with those of (I) and also (V) [the spectrum of (V) has been recorded in Table II for comparison].

It has been reported that (IX) and its *p*-tolyl analogue, when heated with ammonia in a sealed tube, undergo isomerisation to (V) and its tolyl analogue (Kurzer, *Chem. Ind.*, 1956, 528 ; Dixit, *loc. cit.*). Such an isomeric change from a compound with the structure of the type (G) (with two phenyl groups less) to (D) is difficult to conceive. With a structure of the type (H) it may, however, possibly isomerise to a thiadiazole structure (akin to V) by snapping of the bond between sulphur and benzene nucleus, followed by rearrangement. Since the isomeric (I) (A) is already known, (IX) is not likely to have a structure analogous to (G) or (H). It is probable that it has a 1 : 2 : 4-thiadiazole structure, identical with the one suggested by Dost (*Ber.*, 1906, **39**, 863) (VA), which can simply isomerise to (VB).

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# AMINO DERIVATIVES OF TUNGSTEN(VI) CHLORIDE. PART I

By Sarju Prasad and K. S. R. Krishnaiah

The amino derivatives of tungsten(VI) chloride have been prepared by the action of tungsten(VI) chloride on some mono- and di-amines, their properties studied and structures discussed.

Spacu (*Bull. Sect. Sci. Acad. Roumaine*, 1940, **22**, 329) studied $WCl_6$—ammonia system tensimetrically at—75°; he removed associated ammonia at various temperatures up to 0° and observed the formation of $WCl_6.6NH_3$. Fowles and Osborne (*J. Chem. Soc.*, 1959, 2275) prepared $WCl_6.4NH_3$ and $WCl_6.6NH_3$ by passing dry ammonia gas through a solution of $WCl_6$ in $CCl_4$, and observed the formation of various ammono basic tungsten(VI) chlorides by subsequent ammonolysis of the compounds.

The present investigation was undertaken with a view to studying the formation of compounds by treating tungsten(VI) chloride with aromatic primary mono- and di-amines in $CCl_4$.

## Experimental

The amines used were of Merck's or B. D. H. 'extra pure' quality. Carbon tetrachloride ("Analar") was dried over and distilled from $P_2O_5$ immediately before use.

Tungsten(VI) chloride was prepared by the action of chlorine on pure tungsten powder (Messrs. Johnson and Matthey) at 600° in a quartz tube in the complete absence of oxygen. Traces of tungsten(VI) oxychlorides were also formed but were sublimed off. Excess of chlorine was removed by passing dry deoxidised nitrogen. A solution of tungsten(VI) chloride, dissolved in $CCl_4$, was used in all the experiments.

*Procedure.*—A dilute solution of the amine in dry $CCl_4$ was slowly added to tungsten(VI) chloride solution with constant shaking till complete precipitation, leaving the amine in slight excess. The product was transferred to a sintered glass funnel and washed with dry $CCl_4$ till free of amine, all these operations having been carried out in a nitrogen atmosphere. Finally the product was dried in vacuum.

A weighed quantity of the compound was digested with $HNO_3$ (conc.) for several hours on a water bath. It was then evaporated to dryness, ignited, and weighed as $WO_3$.

Chlorine was estimated by Piria and Schiff's method as AgCl, and nitrogen by Kjeldahl's method.

The compounds of tungsten(VI) chloride with mono- and diamines prepared are listed in Tables I and II.

*General Properties.*—All the compounds are coloured, insoluble in $CCl_4$, ether, benzene, and acetone but sparingly soluble in ethanol; these are fairly stable in dry atmosphere but, when exposed to moist air, absorb moisture and decompose. When heated, these compounds decompose before melting. The aqueous extract of the compounds responds to the test for chlorine showing thereby that chlorine is in an ionisable state. The compounds formed with diamines are

comparatively stable with respect to those with monoamines, due probably to chelation. These are decomposed by acids and alkalies. On heating with soda lime, the corresponding amines separate out and condense on the cooler parts of the test tube. All the compounds respond to the diazo test.

## TABLE I

*With primary monoamines.*

| | Amine. | Compound formed. | Colour | % Tungsten. Found. | % Tungsten. Calc. | % Chlorine. Found. | % Chlorine. Calc. | % Nitrogen. Found. | % Nitrogen. Calc. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | Aniline | $[W(C_6H_5NH_2)_6]Cl_6$ | Grey | 19.45 | 19.27 | 22.30 | 22.28 | 8.73 | 8.80 |
| 2. | α-Naphthylamine | $[W(C_{10}H_7NH_2)_6]Cl_6$ | Bluish grey | 14.72 | 14.66 | 16.88 | 16.95 | 6.65 | 6.69 |
| 3. | β- ,, | ,, | Do | 14.60 | ,, | 16.96 | ,, | 6.65 | ,, |
| 4. | *o*-Toluidine | $[W(CH_3.C_6H_4NH_2)_6]Cl_6$ | Light ash | 17.64 | 17.71 | 20.50 | 20.48 | 8.03 | 8.09 |
| 5. | *m*- ,, | ,, | Do | 17.80 | ,, | 20.42 | ,, | 8.05 | ,, |
| 6. | *p*- ,, | ,, | Light brown | 17.72 | ,, | 20.36 | ,, | 8.07 | ,, |
| 7. | *o*-Anisidine | $[W(CH_3O.C_6H_4NH_2)_6]Cl_6$ | Boluish grey | 16.40 | 16.21 | 18.53 | 18.75 | 7.41 | 7.40 |
| 8. | *m*- ,, | ,, | Blue | 16.12 | ,, | 18.70 | ,, | 7.37 | ,, |
| 9. | *p*- ,, | ,, | Bluish grey | 16.34 | ,, | 18.55 | ,, | 7.39 | ,, |
| 10. | *o*-Phenetidine | $[W(C_2H_5O.C_6H_4NH_2)_6]Cl_6$ | Dirty grey | 15.10 | 15.09 | 17.56 | 17.45 | 6.88 | 6.90 |
| 11. | *m*- ,, | ,, | Light brown | 15.26 | ,, | 17.40 | ,, | 6.89 | ,, |
| 12. | *p*- ,, | ,, | Light grey | 15.18 | ,, | 17.46 | ,, | 6.87 | ,, |
| 13. | Benzylamine | $[W(C_6H_5.CH_2NH_2)_6]Cl_6$ | Pale yellow | 17.62 | 17.71 | 20.53 | 20.48 | 8.08 | 8.10 |

## TABLE II

*With diamines.*

| | Amine. | Compound formed. | Colour. | % Tungsten. Found. | % Tungsten. Calc. | % Chlorine. Found. | % Chlorine. Calc. | % Nitrogen. Found. | % Nitrogen. Calc. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | Benzidine | $[W(NH_2C_6H_4{-}C_6H_4NH_2)_3]Cl_6$ | Grey | 19.58 | 19.39 | 22.32 | 22.42 | 8.83 | 8.855 |
| 2. | *o*-Tolidine | $[W(CH_3.NH_2C_6H_3{-}C_6H_3NH_2CH_3)_3]Cl_6$ | Bluish grey | 17.77 | 17.81 | 20.54 | 20.60 | 8.12 | 8.135 |
| 3. | *o*-Phenylenediamine | $[W\{C_6H_4(NH_2)_2\}_3]Cl_6$ | Reddish brown | 25.28 | 25.52 | 29.64 | 29.52 | 11.62 | 11.66 |
| 4. | *m*- ,, | ,, | Greenish grey | 25.46 | ,, | 29.56 | ,, | 11.64 | ,, |
| 5. | *p*- ,, | ,, | Light grey | 25.60 | ,, | 29.50 | ,, | 11.64 | ,, |
| 6. | Dimethyl-*p*-phenylenediamine | $[W\{C_6H_4(NHCH_3)_2\}_3]Cl_6$ | Dark brown | 22.64 | 22.85 | 26.70 | 26.44 | 10.43 | 10.44 |
| 7. | *m*-Toluylenediamine | $[W\{CH_3.C_6H_3(NH_2)_2\}_3]Cl_6$ | Light blue | 24.20 | 24.12 | 27.90 | 27.89 | 10.99 | 11.01 |
| 8. | Dianisidine | $(W\{CH_3O(NH_2)C_6H_3{-}C_6H_3(NH_2)OCH_3\}_3]Cl_6$ | Dirty pink | 16.48 | 16.29 | 18.62 | 18.85 | 7.42 | 7.44 |
| 9. | Phenylhydrazine | $(W(C_6H_5NH.NH_2)_3]Cl_6$ | Buff | 25.38 | 25.52 | 29.62 | 29.52 | 11.62 | 11.65 |

## DISCUSSION

The effective atomic number of tungsten in these compounds is 80, which is not a stable configuration, and therefore the compounds, though stable in the dry atmosphere at the room temperature, begin to hydrolyse slowly on exposure to moist air, or when treated with water, dilute NaOH or dilute $Na_2CO_3$ solution.

In all the cases studied, six molecules of a monoamine or three molecules of a diamine attach themselves to one molecule of tungsten(VI) chloride. It appears that the amines attach themselves to the central atom, chelete compounds being formed in the case of diamines, and may be represented as $[W(6A)]Cl_6$, where A is a primary monoamine, and $[W(3D)]Cl_6$, where D is a diamine.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

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# PREPARATION OF SOME NEW ACID HYDRAZIDES AND HYDRAZONES

BY BRIJRAJ SINGH RATHORE AND P. I. ITTYERAH

The preparation of the hydrazides of malonanilic, malon-*o*-, -*m*- and -*p*-toluidic, and malon-*o*-, -*m*- and -*p*-chloroanilic acids is described. Malon-*o*-chloroanilic acid hydrazide has been used to prepare the corresponding hydrazones from various aldehydes and ketones.

Acid hydrazides find considerable use in chemotherapy, and such compounds in large number have been prepared and their properties investigated by earlier workers. Yale *et al.* (*J. Amer. Chem. Soc.*, 1953, **75,** 1933) have described the preparation of a number of new hydrazides, but their emphasis has been on the *iso*nicotinic acid hydrazide type, with a view to establishing the structural requirements for antituberculous activity.

This communication deals with the preparation of the hydrazides of a number of malonic acid derivatives, and the use of one of these for the preparation of hydrazones from aldehydes and ketones. Malonanilic acid, the three malontoluidic acids, and the three malonchloroanilic acids have been chosen for this purpose. The ethyl esters of these acids were prepared by a slight modification of the method described by Chattaway and Olmsted (*J. Chem. Soc.*, 1910, **97,** 940). The ethyl esters of malon-*o*- and -*m*-chloroanilic acids have been isolated in pure condition for the first time. The other esters were prepared by earlier workers.

The method employed for the preparation of the acid hydrazides is more or less the same as the one adopted by Yale *et al.* (*loc. cit.*). The yield m.p., etc. of the hydrazides obtained are shown in Table I.

Further investigations show that these acid hydrazides can be used as reagents for detection of carbonyl compounds. These readily form crystalline hydrazones with a number of aldehydes and ketones. Several hydrazones were prepared using malon-*o*-chloroanilic acid hydrazide. The general procedure has been to take equimolecular quantities of the aldehyde or ketone and the acid hydrazide in ethanolic solution, and to keep the mixture at room temperature for 15 to 30 minutes. In the case of chloral it was observed that in ethanolic solution the product formed had a nitrogen content higher than what was expected, and it melted with decomposition at 221°. The identitiy of the compound could not be established. When dry benzene was used in place of ethanol and the mixture refluxed for 30 minutes, the expected hydrazone crystallised out. The m.p., yield, etc. of the hydrazones are recorded in Table II.

The ketones were slower to react than the aldehydes. Under the conditions tried, *n*-heptaldehyde, 5-nitrothiophen-2-aldehyde, acetone and benzophenone did not react.

## EXPERIMENTAL

*Ethyl Malon-o-chloroanilate.*—A mixture of *o*-chloroaniline (5 g.) and ethyl malonate (10 g.) was refluxed for 30 minutes in a r.b. flask fitted with an air condenser of such a length that the ethanol formed could escape, allowing ethyl malonate to flow back into the flask. The contents were allowed to cool, ethanol (30 c.c.) added, and the crystals of malon-di-*o*-chloroanilide separating were filtered off. The filtrate containing malon-*o*-chloroanilate was added slowly with stirring to 500 c.c. of water. The ester, which was precipitated as a pale yellow solid, was filtered off and recrystallised from petroleum ether (b.p. 60-80°) in colorless crystals, m.p. 60°, yield 3.5 g. (36.8%). (Found : N, 5.38. $C_{11}H_{12}O_3NCl$ requires N, 5.79%).

Similarly ethyl malonanilate (m.p. 39°, yield 40%), ethyl malon-*o*-toluidate (m.p. 73°, yield 13.2%), ethyl malon-*p*-toluidate (m.p. 85°, yield 44.7%), ethyl malon-*m*-chloroanilate (m.p. 74°, yield 31.6% ; found : N, 6.13 ; $C_{11}H_{12}O_3NCl$ requires N, 5.79%), and ethyl malon-*p*-chloroanilate (m.p. 92-94°, yield 44.7%) were prepared. Ethyl malon-*m*-toluidate was obtained as a viscous liquid, and this was found pure enough for the subsequent step. Other esters were prepared as above.

*Malon-o-chloroanilic Acid Hydrazide.*—85% Hydrazine hydrate (1 c.c.) was added to a solution of ethyl malon-*o*-chloroanilate (2 g.) in ethanol (5 c.c.). The reaction was spontaneous. The contents became slightly warm and the hydrazide crystallised out in colorless needles. The flask was set aside for 30 minutes. The solid mass was dissolved in hot ethanol (20 c.c.) and this on cooling deposited pure crystals of malon-*o*-chloroanilic acid hydrazide, m.p. 128°, yield 1.53 g. (81.2%). Other hydrazides were prepared similarly.

The purification of malonanilic acid hydrazide and malon-*m*-toluidic acid hydrazide was tedious. These could, however, be obtained pure by repeated extraction with boiling water in which the hydrazides are soluble.

TABLE I

*New acid hydrazides.*

| Compounds. | M. P. | Yield. | Formula. | % Nitrogen. | |
|---|---|---|---|---|---|
| | | | | Found. | Calc. |
| Malonanilic X* | 186° | 67.0% | $C_9H_{11}O_2N_3$ | 22.23 | 21.76 |
| Malon-*o*-toluidic X | 136° | 66.19 | $C_{10}H_{13}O_2N_3$ | 19.90 | 20.29 |
| Malon-*m*-toluidic X | 168° | 35.02 | $C_{10}H_{13}O_2N_3$ | 20.40 | 20.29 |
| Malon-*p*-toluidic X | 182° | 64.60 | $C_{10}H_{13}O_2N_3$ | 19.92 | 20.29 |
| Malon-*o*-chloroanilic X | 128° | 81.21 | $C_9H_{10}O_2N_3Cl$ | 18.49 | 18.49 |
| Malon-*m*-chloroanilic X | 179° | 87.20 | $C_9H_{10}O_2N_3Cl$ | 19.16 | 18.49 |
| Malon-*p*-chloroanilic X | 188° | 66.34 | $C_9H_{10}O_2N_3Cl$ | 18.64 | 18.49 |

*X stands for acid hydrazide.

TABLE II

*New hydrazones.*

| Hydrazone. | M. P. | Yield. | Formula. | % Nitrogen. | |
|---|---|---|---|---|---|
| | | | | Found. | Calc. |
| Furfuraldehyde-R* | 196° | 88.4% | $C_{14}H_{12}O_3N_5Cl$ | 14.01 | 13.74 |
| Thiophen-2-aldehyde-R | 168° | 49.1 | $C_{14}H_{12}O_2N_5ClS$ | 13.62 | 13.06 |
| Chloral-R | 178° | 27.6 | $C_{11}H_9O_2N_5Cl_4$ | 11.82 | 11.76 |
| Benzaldehyde-R | 193° | 86.5 | $C_{15}H_{14}O_2N_5Cl$ | 13.02 | 13.31 |
| o-Chlorobenzaldehyde-R | 208° | 93.6 | $C_{15}H_{13}O_2N_5Cl_2$ | 11.93 | 12.00 |
| 5-Chlorosalicylaldehyde-R | 213° | 87.0 | $C_{15}H_{13}O_3N_5Cl_2$ | 11.21 | 11.48 |
| 5-Bromosalicylaldehyde-R | 218° | 99.7 | $C_{15}H_{13}O_3N_5ClBr$ | 10.69 | 10.23 |
| 3:5-Dibromosalicylaldehyde-R | 214° | 82.7 | $C_{15}H_{12}O_3N_5ClBr_2$ | 9.04 | 8.58 |
| 3:5-Diiodosalicylaldehyde-R | 221° | 81.1 | $C_{15}H_{12}O_3N_5ClI_2$ | 7.33 | 7.19 |
| 3-Nitrosalicylaldehyde-R | 206° | 92.4 | $C_{15}H_{13}O_5N_6Cl$ | 14.83 | 14.87 |
| 5 Nitrosalicylaldehyde-R | 222° | 83.4 | $C_{15}H_{12}O_5N_6Cl$ | 15.14 | 14.87 |
| 3:5-Dinitrosalicylaldehyde-R | 208° | 85.7 | $C_{15}H_{12}O_7N_7Cl$ | 16.84 | 16.61 |
| 3-Nitro-5-chlorosalicylaldehyde-R | 210° | 94.4 | $C_{15}H_{12}O_5N_6Cl_2$ | 13.05 | 13.62 |
| 3-Nitro-5-bromosalicylaldehyde-R | 204° | 88.8 | $C_{15}H_{12}O_5N_6ClBr$ | 12.36 | 12.29 |
| Salicylaldehyde-R | 199° | 89.8 | $C_{15}H_{14}O_3N_5Cl$ | 12.44 | 12.67 |
| Methylethyl ketone-R | 150° | 44.5 | $C_{13}H_{16}O_2N_5Cl$ | 15.32 | 14.90 |
| Acetophenone-R | 191° | 61.5 | $C_{17}H_{16}O_2N_5Cl$ | 12.66 | 12.75 |

*R stands for malon-o-chloroanilic acid hydrazone.

*Hydrazones.*—In the case of liquid aldehydes, the acid hydrazide was dissolved in the minimum quantity of cold ethanol and an equimolecular quantity of the aldehyde was added. The mixture was kept aside for about 30 minutes, and then the hydrazone separating was filtered and recrystallised from ethanol.

In the case of solid aldehydes, the acid hydrazide and the aldehyde were taken in ethanol and warmed till a homogeneous solution was obtained. It was set aside and extracted as before.

In the case of ketones, the mixture was refluxed for 1-2 hours.

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# SHORT NOTES

## PREPARATION OF THE FORMATES OF RARE EARTH ELEMENTS

By Balaram Sahoo, S. Panda and D. Patnaik

A convenient method for the preparation of formates of the rare earth elements is not available in the literature. The method adopted by us involves the reaction of the nitrates of the desired elements with formic acid. The formates are easily obtained by this method, and these contain 0.25 molecules of water of hydration.

The nitrates of lanthanum and cerium used were of E. Merck 'extrapure' quality and that of thorium used was of B.D.H. Analar quality. Formic acid of E. Merck 'extrapure' quality was used. Since the reaction of nitrates of these elements with formic acid was vigorous, the nitrates were added in small quantities at a time to 20 c.c. of formic acid taken in a flask. When evolution of gases involving nitrous fumes had ceased, a considerable quantity of salt was formed. The formates settled down in granular form. The supernatant liquid was decanted off and the precipitate was again refluxed for 2 hours with a fresh quantity of formic acid. The precipitates were filtered off and kept in a vacuum desiccator over solid caustic soda. In case of the thorium formate, heating the precipitate at 80-90° under vacuum was carried out. The compounds have been tested to be free from nitrogen.

The oxide content after ignition was determined as described previously (Patnaik and Panda, *Curr. Sci.*, 1956, **25**, 287). For the estimation of the formate content the method adopted was first to dissolve a weighed quantity of the salt in a fixed volume of $N/10$-$H_2SO_4$. Then $N/10$-NaOH solution was added in slight excess of the volume required for bringing about complete hydrolysis. After heating to boiling, the hydroxide of the rare earth was filtered off. The solution was next acidified with $H_2SO_4$ and again made alkaline with solid $Na_2CO_3$ after which the estimation was carried out according to the standard method.

It is not possible to determine directly the associated water by the method of Brush and Penfield as the compounds undergo decomposition on heating. Attempt was made to determine the water content by the method of isothermal dehydration. It was found that up to 90° water could not be completely removed and when the dehydration was carried above 90°, decomposition of the compound started. Therefore semimicro combustion method was adopted for the estimation of total hydrogen and carbon. This would give an extra amount of 1.5 mole of water for each mole of lanthanum and cerous formates and 2 moles of water per mole of thorium formate, resulting from the decomposition of the formate groups, in addition to the associated water. The experimental results along with the calculated values of the formates, assuming to be associated with 0.25 molecules of water, agree quite satisfactorily within the limits of experimental error.

The presence of a small fractional number of water molecules in such heavy metal formates makes it beyond the scope of experiment to rigidly decide that the number of hydration should be 0.25. Without any detriment to the permissible percentage of error of the various experimental data, the number of water of crystallisation may lie within the range 0.25 to 0.30. Of all the analyses for the constituents of the hydrated formate, the determination of metallic oxide is the most accurate one, and so in consideration of this fact, we are in favour of 0.25 molecules of water to be associated with each molecule of the rare earth formate.

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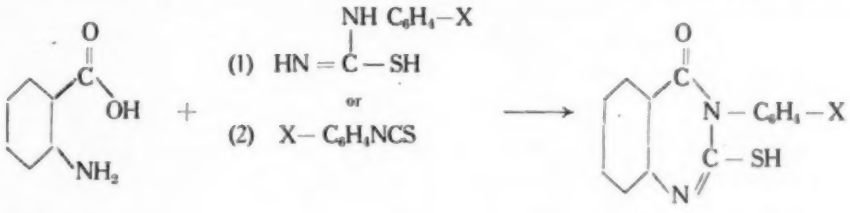
*Received July 30, 1956.*

# 2-MERCAPTO-3-SUBSTITUTED PHENYLQUINAZOL-4-ONES

By G. R. Dave, G. S. Mewada and G. C. Amin

The quinazolone derivatives, studied by several workers (Baker *et al.*, *J. Org. Chem.*, 1953, **18**, 78 ; Bami and Dhatt, *J. Sci. Ind. Res.*, 1957, **16B**, 558 ; 1959, **18C**, 256 ; Sen and Singh, this *Journal*, 1959, **36**, 787, 807 *et seq*), are recently receiving more attention as potential antimalarials. Only a few quinazolone derivatives are, however, known containing sulphur atom in the molecule (Elderfield, "Heterocyclic Compounds", John Wiley and Sons, Inc., New York, Vol. VI, 1956, p.369). 2-Mercapto-3-phenyl- and -3-tolyl-quinazol-4-ones have been described in literature (McCoy, *Ber.*, 1897, **30**, 1688 ; Pawlewski, *Ber.*, 1905, **38**, 131 ; Ghosh, this *Journal*, 1930, **7**, 981). In the present communication several 2-mercapto-3-substituted phenylquinazol-4-ones have been synthesised by two general methods outlined below. The compounds are listed in Table I.




(II) (I)

(*i*). A mixture of 2-aminobenzoic acid (II, 1 *M*) and monosubstituted thiourea (1 *M*) was heated at 180-90° for about 2 hours, keeping a long tube as condenser. On cooling, the reaction mass was treated with water, followed by a 10% NaOH solution. The alkaline solution was filtered, and the filtrate acidified with HCl, when 2-mercapto-3-substituted phenylquinazol-4-ones (I) separated.

(*ii*). A solution of 2-aminobenzoic acid (II, 1 *M*) and aryl *iso*thiocyanate (1 *M*) in sufficient quantity of ethanol was refluxed on a water bath for about 1½ hrs. The product, separating on cooling and dilution, was extracted with alkali. 2-Mercapto derivative was obtained as in (*i*).

TABLE I

| (I : X=). | M. P. | Formula. | % Sulphur. | |
|---|---|---|---|---|
| | | | Found. | Calc. |
| 2-OMe | 253° | $C_{15}H_{13}O_2N_2S$ | 10.94 | 11.26 |
| 4-OMe | 284° | $C_{15}H_{13}O_2N_2S$ | 11.03 | 11.26 |
| 2-Cl | 268° | $C_{14}H_9ON_2ClS$ | 10.81 | 11.09 |
| 3-Cl | 291° | $C_{14}H_9ON_2ClS$ | 10.78 | 11.09 |
| 4-Cl | 253° | $C_{14}H_9ON_2ClS$ | 11.03 | 11.09 |
| 2-$NO_2$ | 234° | $C_{14}H_9O_3N_3S$ | 10.31 | 10.70 |
| 3-$NO_2$ | 262° | $C_{14}H_9O_3N_3S$ | 10.43 | 10.70 |
| 4-$NO_2$ | 287° | $C_{14}H_9O_3N_3S$ | 10.55 | 10.70 |
| 2-COOH | 288° | $C_{15}H_{10}O_3N_2S$ | 10.43 | 10.74 |
| 4-$SO_3H$ | 291° | $C_{14}H_{10}O_4N_2S_2$ | 18.93 | 19.17 |

All the compounds were crystallised from acetone as colorless plates, after treatment with charcoal.

The preparation of the other Bz-substituted quinazolones and study of the reactivity of these compounds are under progress.

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CHEMISTRY DEPARTMENT,
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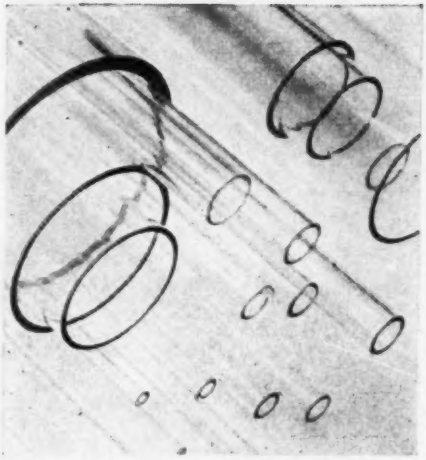

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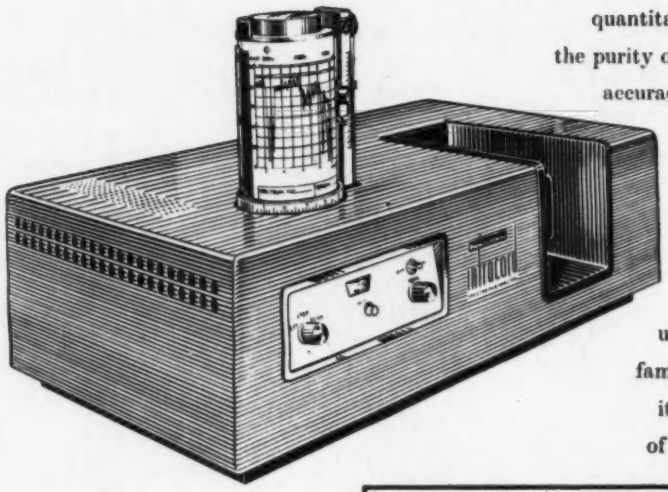


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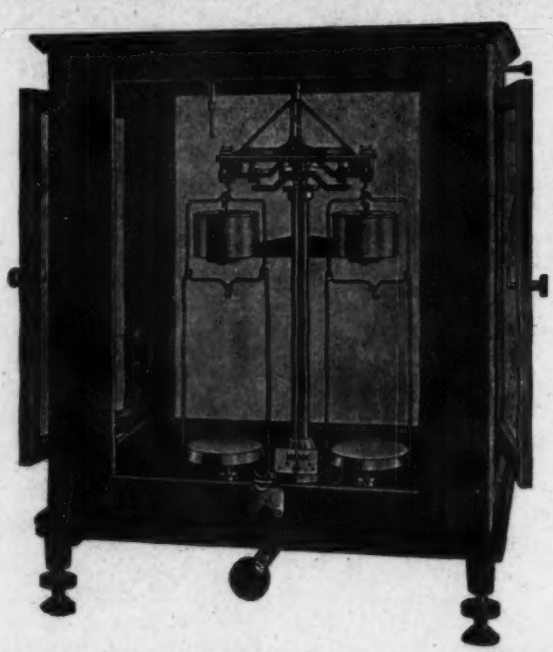

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